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Thesis

THE USE OF TITANOUS CHLORIDE IN THE REDUCTION OF ORGANIC COMPOUNDS

by

Harvey Roosevelt Engle
(A.B., Hiram College, 1932)

submitted in partial fulfillment of the
requirements for the degree of
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1934

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I INTRODUCTION

The quantitative reactions of titanous chloride are of especial interest because they have been so widely applied. This paper will be confined to the reactions with organic compounds only, except where inorganic reactions enter into the standardization of reagents used. The quantitative reactions are of greater importance, but other reactions of interest will be discussed. Although titanous sulfate has come into common use especially in this country, the chloride still occupies a very important place in quantitative analytical determinations.

A brief review of the literature of the field will be given. Proven analytical methods will be outlined and their results evaluated. Some of them will be checked in the experimental part of the paper. Ceric sulfate will be recommended as a secondary standard.

There are only a few good reducing agents in use in volumetric analysis. Of these thiosulfate and arsenious oxide are the only ones whose aqueous solutions are stable in the air. Titanous chloride is a very powerful reducing agent and hence fills an important place in volumetric analysis.

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Credit is given to Gregor, an English clergyman, for the first account of the occurence of titanium. He found it in a mineral then known as menakanite but did not isolate it. He prepared titanous sulfate solutions and described some of their properties. This was published in 1791. Berzelius isolated the element much later.

In 1847, Ebelman (1), in describing the reactions of titanous chloride, first called attention to the fact that its aqueous solution had strong reducing properties. He pointed out that it was capable of reducing the salts of iron and copper to their lowest states of oxidation. As more was learned of the properties of the compound it became increasingly more important as a volumetric reagent.

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II REVIEWS AND DISCUSSIONS OF THE LITERATURE

A. The Work of E. Knecht and E. Hibbert.

Edmund Knecht (1) first applied titanous chloride extensively as a reducing agent in the quantitative estimation of both inorganic and organic compounds. He and Eva Hibbert, with whom much of the work was done, have published a book (2) which includes most of the important work done in the field up until 1925.

In the early work with titanous chloride, the solution had to be prepared in the laboratory. Hence, in the early articles Knecht (1) gives directions for the preparation. He mentions three ways to prepare solutions pure enough for analytical work:

1) Reduction of titanium tetrachloride with zinc, precipitation of the zinc with hydrogen sulfide gas, filtration, and then dilution to strength. In later work (2) aluminum, copper, and mercury were also used.

2) Reduction of the purified tetrachloride with pure zinc dust and the use of the solution directly.

3) Electrolytic reduction of the titanium tetrachloride or the double decomposition of the electrolytically prepared titanium sulfate with barium chloride.

(1) E. Knecht, Ber., 36(1), 166,(1903)
(2) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" Second Edition (1925) Longmans, Green, and Co., London.

The anhydrous salt may be prepared by passing the titanium tetrachloride in the vapor state with hydrogen through a red-hot tube. Hydrochloric acid is formed with the titanous chloride. The titanous chloride is deposited in the cooler parts of the tube in the form of dark violet scales which deliquesce in the air forming a red-violet liquid.

The aqueous solution may be readily prepared by dissolving titanium metal in strong hydrochloric acid. The metal dissolves readily forming a blue solution while hot which turns purple on cooling. The solution can easily be diluted to the desired strength. Concentrated solutions may be prepared from dilute solutions by evaporation under reduced pressure and preferably in an atmosphere which is inert.

The solution appears on the market as a 15 to 20 percent solution in strong hydrochloric acid. The main impurity is ferrous iron. This does not interfere with the usual methods of standardization using iron salts nor with those determinations in which the back titration is with iron alum. Ferrous iron is undesirable when potentiometric methods are used. If the ferrous iron is capable of reducing the compound which is being estimated, it will cause an error in a direct titration of the compound with titanous chloride if the titanous chloride solution has been standardized with a ferric salt. Good grade preparations which are nearly iron free are on the market now.

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Polidori (1) obtained a pure compound free from iron by precipitation of the titanous chloride with gaseous hydrogen chloride. In his method gaseous hydrogen chloride is bubbled thru an acidified commercial solution of the titanium chloride in a closed container which is cooled in an ice-salt mixture. Several days are required for the complete precipitation of the violet $TiCl_3 \cdot 6$ HOH crystals. The crystals are collected quickly and washed with ice-cold hydrochloric acid. A 20 percent solution in 20 percent hydrochloric acid is prepared directly so that the air has little chance to act on the titanous salt.

Knecht (2) found that the nitro group was quantitatively reduced to the amino group by boiling with a dilute acid solution of titanous chloride in excess. Dinitrobenzene (2) gave m-nitraniline when the amount of the reducing agent was held to six equivalents which is the amount required for the reduction of one nitro group. Thus one nitro group could be reduced in the presence of another. Various organic acids were found to be slowly reduced. Oleic acid (2) gave stearic acid; fumaric acid gave succinic; citraconic gave pyrotartaric. These reductions of fatty acids were not quantitative. Titanous sulfate was found to behave similarly but was found to be insoluble in alcohol.

(1) Polidori, Z. anorg. allgem. Chem., 19, 306 (1899)
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(2) K. Knecht, Ber., 36, 166, (1903)

In ammoniacal solution when the sesquioxide or hydrate was really present, azobenzene (1) was reduced to hydrazobenzene. Berliner blue became colorless even when dyed on cloth and subjected to reduction. It became blue on exposure to air again. These preliminary experiments showed the importance of the salt as a reducing agent in volumetric analysis. Therefore Knecht refined his technique and built an apparatus which would exclude air from the reduction solution. (See illustration in III Standard Methods)(Page 42)

The solution was kept in a bottle with an opening in the top and one in the side at the bottom. The neck opening was fitted with a two-hole stopper, one hole for the entrance of hydrogen supplied by a small testtube generator and the other connected to the top of the burette in order to equalize the pressure. The lower opening held a glass tube by which the burette was filled, there being a T connection one end of which was fastened to the burette and the other end held the bead valve. (2) The whole was supported so that the top of the burette was just below the bottom of the bottle. In this arrangement the burette was easily filled by gravity. The apparatus will be described in detail in a later part of the paper.

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An approximately 0.03 normal solution was prepared by boiling 50 ml. of the commercial 20 % solution with 50 ml. of concentrated hydrochloric acid. Later the amount of the acid was doubled to increase stability of the solution. The solution was cooled and made up to 2¼ liters in the storage bottle. The solution was standardized with pure ferrous ammonium sulfate in dilute sulfuric acid solution. The ferrous salt was oxidized with nitric acid in the original procedure. (1) At Yates' suggestion potassium permanganate was substituted for this oxidation. The endpoint of the reduction was determined by the spot test with potassium or ammonium thiocyanate. Ammonium thiocyanate was preferred because it costs less. It was found that much time could be saved by adding the indicator directly to the solution and that the results were not affected.

In the estimation of a compound, a known amount of the compound was boiled for from five to ten minutes with an excess of titanous chloride in a flask into which was kept running a stream of carbon dioxide which kept the reducing agent from being acted on by the air. (1) (2) (3)

(1) E. Knecht, J.S.D.and C., 19, 169 (1903)
(2) E. Knecht, Ber., 36, 1549 (1903)
(3) E. Knecht and Eva Hibbert,
"New Reduction Methods in Volumetric Analysis"
Second edition (1925). Longmans, Green and Co., London.

An approximately 0.03 normal solution was prepared by boiling 30 ml. of the commercial 20 % solution with 80 ml. of concentrated hydrochloric acid. Later the amount of the acid was doubled to increase stability of the solution. The solution was cooled and made up to 2½ litres in the storage bottle. The solution was standardized with pure ferrous ammonium sulfate in dilute sulfuric acid solution. The ferrous salt was oxidized with nitric acid in the original procedure. (1) At Yates' suggestion potassium permanganate was substituted for this oxidation. The endpoint of the reduction was determined by the spot test with potassium or ammonium thiocyanate. Ammonium thiocyanate was preferred because it costs less. It was found that much time could be saved by adding the indicator directly to the solution and that the results were not affected.

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The excess of the reducing agent was then titrated with a standard solution of ferric alum containing 14 grams of the salt per liter and strongly acidified with sulfuric acid to prevent the precipitation of basic salts. Potassium or ammonium thiocyanate, about 10 ml. of a 10 % solution, was added for an indicator. The organic compound was calculated from the corrected titer of titanous chloride.

Phenylazo-beta-naphthol dissolved in fuming sulfuric acid and made up to a dilute solution gave 100.2 %. Sulfonated on a water-bath for an hour and a half and then estimated, it gave 99.8 %. Picric acid was easily reduced. It required eighteen equivalents. The azo dyes were found to be quantitatively reduced. Orange II and benzopurpurin were estimated accurately. The method was found to be much more accurate than the standard methods for the estimation of dyes. Nitrobenzene was sulfonated so as not to be volatile with steam and gave good results. (1) Of course ferric iron must not be present in the dye solution. Crystal scarlet and cotton scarlet gave theoretical results. Compounds not easily sulfonated which were insoluble in water were dissolved in alcohol and the alcoholic solution slowly added to the reduction mixture while it was kept near boiling. (2)

(1) E. Knecht, Ber., 36 (1), 1549 (1903)
(2) E. Knecht, J. S. D. and C., 19, 169 (1903)

Many of the dyes are titrated directly. If hydrochloric acid precipitates the dye or if the reduction proceeds slowly, excess titanous chloride is added and after boiling for from two to ten minutes, the excess is titrated with standard iron alum as in the usual procedure with nitro compounds.

Knecht estimated the amount of dye in dyed cloth by the method. (1) The active chlorine in the cloth was removed with sodium thiosulfate. Extraction of the dye was tried with alcohol and glycerine but the method was found unsatisfactory. The method finally recommended was boiling with excess of the reducing agent right after the removal of the chlorine and with the dye yet on the cloth. The excess was titrated as in the usual procedure with standard iron alum solution.

Methylene blue was titrated directly with titanous chloride and the method was found so convenient that the reaction was recommended for its standardization. (2)
The dyes of the triphenylmethane series were estimated by the usual method using iron alum. Heavy precipitates often obscured the end-point. This was remedied by the addition of Rochelle salt. (3)

(1) J. S. D. and C., 21, 3 (1905)
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(3) J. S. D. and C., 21, 111 (1905)

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Indigo, p-rosaniline hydrochloride, p-rosaniline trisulfonic acid, crystal violet, malachite green, tolusafranine, and eosin were found to be quantitatively reduced and the end-point to be satisfactory in the back titration with iron alum if Rochelle salt was present. (1) Sodium tartrate was later substituted for the mixed salt and was found to give better results. (2)

Polynitro compounds were found to often yield only about 90 % reduction. These compounds were successfully estimated by the usual procedure only when a great excess of titanous chloride was added and the solution boiled for at least 5 minutes. Methylene blue was used as the indicator in these titrations. (3) The end-point must be approached slowly unless the solution is heated to 40 degrees. One drop of a ten percent solution of sodium salicylate may be used in place of the heating. Lauterbach suggested the use of salicylic acid. (4)

Nitroso compounds were found to be quantitatively reduced to the corresponding amino compounds. The reaction is carried out at from 40 to 60 degrees. (5) The direct method is used if the nitroso compound is deeply colored in solution. If desired, methylene blue may be used for the

(1) J. S. D. and C., 21, 292 (1905)
(2) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" IIed. p.65. (1925) Longmans, Green, and Co., London
(3) E. Knecht and E. Hibbert, Ber., 40(3), 3819 (1907)
(4) E. Knecht and E. Hibbert, op. cit.,(note2) p64
(5) E. Knecht and E. Hibbert, ibid., p32.

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Polynitro compounds were found to often yield only about 80 % reduction. These compounds were successfully estimated by the usual procedure only when a great excess of titanous chloride was added and the solution boiled for at least 5 minutes. Methylene blue was used as the indicator in these titrations. (3) The end-point must be approached slowly unless the solution is heated to 40 degrees. One drop of a ten percent solution of sodium salicylate may be used in place of the heating. Lauterbach suggested the use of salicylic acid. (4)

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(4) K. Knecht and E. Hibbert, op. cit.,(Note) p64
(5) K. Knecht and E. Hibbert, Ibid., p32.

indicator and then the solution need not be cooled as with the back titration with iron alum. It must be remembered that solutions must be cooled to room temperature or below in order that a good end-point color change will be obtained with thiocyanate.

Benzene diazonium chloride was estimated with titanous chloride directly. Alkaline beta-naphthol was used in the spot test as indicator. The reduction product was diazobenzene phenylhydrazide. Two equivalents of titanous chloride were required per mole of chloride. Later it was found preferable to use excess titanous chloride for the reduction, cool, and then back titrate with a standard solution of acid green. The reaction was carried out in the presence of sodium tartrate. (1)

It was found that phenylhydrazine was not reduced by titanous salts. It was estimated by direct titration with methylene blue which had been standardized by titanous chloride. The end-point was slow and not satisfactory, so the procedure finally recommended was that of adding an excess of methylene blue solution and after reduction, to titrate back with titanous chloride solution. p-Nitrophenylhydrazine was found to behave normally yielding p-phenylene diamine and ammonia. Eight equivalents were required. (2)

(1) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" Second edition (1925) p.33. Longmans, Green, and Co., London.
(2) E. Knecht and E. Hibbert, ibid., p. 35.

Willson estimated 2, 4, dinitrophenylhydrazine by reduction with excess titanous chloride and back titration with ferric alum. Fourteen equivalents were required and this amount checked with the theoretical assuming ammonia formed from one nitrogen of the hydrazine group. The ammonia was estimated and was found to agree with the theoretical amount. (1)

Quinones were found to be quantitatively reduced to quinols by titanous chloride in the presence of hydrochloric acid. Both the direct and the indirect methods were used and both gave good results. Methylene blue was used in the direct titration for indicator and this method is to be preferred because it is shorter and more convenient. A list of compounds estimated is given at the end of this section. (2)(p.38)

Knecht had been unable to reduce alpha-nitronaphthalene by his usual procedure. It was commonly believed that chlorination was the cause of the trouble. This was found to be in error. alpha-Nitronaphthalene was found to be quantitatively reduced when a large excess of seven equivalents of hydrochloric acid was present. This amount of acid had to be adhered to rather closely in order to obtain good results. It had been assumed that a chloro-compound was formed but not (3)

(1) E. Knecht and E. Hibbert, New Reduction Methods in Volumetric Analysis" Second Edition (1925) p.36. Longmans, Green, and Co., London.
(2) E. Knecht and E. Hibbert, ibid., p. 40.
(3) E. Knecht, J. C. S., 125 (2), 1537 (1924)

proven. Knecht found no substituted chlorine in the product of the reaction when done under the narrow conditions mentioned. He did prove that one could be formed because he obtained nearly a quantitative yield of 4, chloro-alpha-naphthalene on increasing the amount of hydrochloric acid present to 24 equivalents. (1)

Leigh tried the method of Knecht and Hibbert for the estimation of dye on cloth on alizarin and its lakes. He checked his work against pure alizarin which he prepared pure by subliming in vacuum. In the first method the cloth was boiled with hydrochloricacid protected from the atmosphere by carbon dioxide. Titanous chloride was then run in and the solution boiled for a few minutes. After cooling, the excess titanous chloride was estimated with iron alum using thiocyanate as indicator. In the second method the cloth and dye were dissolved in sulfuric acid and the dye extracted with alcohol. The alcohol solution was then estimated in the usual way. If the products of decomposition of the cloth in sulfuric acid do not affect the titration, the extraction with alcohol can be dispensed with and the sulfuric acid solution diluted and estimated in the usual way. Arsenic compounds were found to interfere. (2) (3)

(1) E. Knecht, J.C.S., 125(2), 1537 (1924)
(2) W. N. Leigh, J.S.D.and C., 32, 205, (1916)
(3) E. Knecht and E. Hibbert, " New Reduction Methods in Volumetric Analysis" Second edition (1925) p. 58 and 111.

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(1) E. Knecht, J.C.S., 1259(2), 1537 (1924)
(2) W. N. Leigh, J.S.D.and C., 32, 205, (1916)
(3) E. Knecht and E. Hibbert, " New Reduction Methods in Volumetric Analysis" Second edition (1925) p. 58 and 111.

In 1924, (1) Knecht and Hibbert published a method for the estimation of glucose and other carbohydrates. It was based on the fact that phenylglucosazone could be estimated accurately by means of titanous chloride. It was found that the glucose was quantitatively converted to the osazone when it was kept near boiling for 10 minutes in a solution which contained 12 mols of phenylhydrazine per mol glucose. As we have seen under the estimation of phenylhydrazine, the excess of that reagent does not enter into the reaction. The reduction products of glucosazone were found to be isoglucosamine, aniline, and ammonia. Six equivalents were required for reduction. Sodium tartrate is added in the reaction. Lactose and maltose work well.

Knecht performed the back titrations in an open conical flask. For very accurate work the flask must be closed and a stream of carbon dioxide must be kept running thru the flask. English and some later workers who used his method even recommend that the carbon dioxide outlet be under water in a separate small flask as an extra precaution to prevent back diffusion of air. (2) A stronger solution of titanous chloride is recommended because it is much more stable. There is less tendency for the oxides to precipitate. Another advantage is that larger samples may be used.

(1) E. Knecht and E. Hibbert, J.C.S., 125, 1537,(1924)
(2) F. L. English, Ind. Eng. Chem., 12, 994, (1920)

In 1924, (1) Knecht and Hibbert published a method for the estimation of glucose and other carbohydrates. It was based on the fact that phenylglucosazone could be estimated accurately by means of titanous chloride. It was found that the glucose was quantitatively converted to the osazone when it was kept near boiling for 10 minutes in a solution which contained 12 mols of phenylhydrazine per mol glucose. As we have seen under the estimation of phenylhydrazine, the excess of that reagent does not enter into the reaction. The reduction products of glucosazone were found to be isoglucosamine, aniline, and ammonia. Six equivalents were required for reduction. Sodium tartrate is added in the reaction. Lactose and maltose work well.

Knecht performed the back titrations in an open conical flask. For very accurate work the flask must be closed and a stream of carbon dioxide must be kept running thru the flask. English and some later workers who used his method even recommend that the carbon dioxide outlet be under water in a separate small flask as an extra precaution to prevent back diffusion of air. (2) A stronger solution of titanous chloride is recommended because it is much more stable. There is less tendency for the oxides to precipitate. Another advantage is that larger samples may be used.

(1) N. Knecht and E. Hibbert, J.C.S., 125, 1357,(1924)
(2) J. L. English, Ind. Eng. Chem., 12, 994, (1920)

B. Miscellaneous Contributions

(1) Standardization of Solutions.

The extensive application of methylene blue to volumetric analysis is largely due to the work of Atack. (1) He did much work on its preparation and purification and on those interfereing substances which are present in the ordinary preparations. He found that it was hard to rid the dye of adsorbed hydrochloric acid if it were crystallized from the ordinary dilute solution of hydrochloric acid. He prepared the free methylene blue base for researches by reduction of an alcoholic solution with phenylhydrazine in an inert atmosphere. This product was also free from chlorine. Due to the presence of a red dye in the technical product the end-point of the titration may be obscured. For this reason he recommends the use of the "medicinal"grade for solutions and for indicator. He outlines five advantages of its use in analysis:

(1) Solution is very stable; fast to light and air. (a 0.5 % solution decreased 0.1 % in three years)
(2) Stable acid solution of the dye and its base.
(3) Easily reduced and easily oxidized back.
(4) High tinctorial value; can use an N/500 solution.
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He standardized his titanous chloride against pure potassium chlorate making up the solution according to Knecht. (2)

(1) Atack, J.S.D.and C., 31, 183, (1915)
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In the standardization, a measured amount of methylene blue solution is run into a conical flask thru which carbon dioxide is kept running. The flask is heated to 40 degrees and just enough titanous chloride added to decolorize the solution. Enough of a standard solution of potassium chlorate is then added to oxidize back approximately half of the leuco base. The methylene blue formed is titrated with titanous chloride in the usual way. The titanous chloride is standardized in terms of oxygen. It can be used then to standardize the methylene blue solution.

Using the above procedure for standardization and the method of Knecht and Hibbert with the slight modification that the back titration waswith methylene blue at 40 degrees, Atack obtained theoretical results with beta-benzildioxime.(1) This procedure eliminates the complete cooling required in the back titration with iron alum. Benzophenoneoxime gave good results by this method. Salvaterra applied the method to the estimation of the nitroso compounds and obtained results comparable to those obtained in the usual procedure. (2) He found that the end-point in the direct titration of those compounds was very hard to recognize and that with many of them there was fading. The back titration with methylene blue was adopted after it was shown that consistent results could be obtained using the method of Knecht and Hibbert only after

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English (1) modified the method of Knecht and Hibbert and applied it in particular to aromatic nitro compounds. His work is accurate and consistent. He showed that even the dissolved oxygen in the water must be removed for accurate work. This was done by boiling for twenty minutes and then cooling in an atmosphere of carbon dioxide. His stock solutions were stronger than Knecht's being 0.05 N and 0.25 N. This allowed the use of larger samples. As we have seen above, the solutions are more stable. His ferric alum solution was 0.05 N. A thermometer was kept in the siphon tube so that the temperature of the solution was known.

Upon standardization with pure ferrous ammonium sulfate which was oxidized with potassium permanganate and then reduced with the titanous chloride, a blank correction of .3 to 0.4 ml. had to be applied to the titer of titanous chloride in order to obtain theoretical results. For this reason, ferrous ammonium sulfate was not recommended for a primary standard. But another factor enters here. Thornton and Chapman have shown that a good grade of ferrous ammonium sulfate is satisfactory for a standard and that it gives but a small error. (2) They also agree with Rhead that (3) the

(1) F. L. English, Ind. Eng. Chem., 12, 994, (1920)
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titer of titanous chloride decreases slightly in strength on heating. Van Duin (1) found the titer of a dilute titanous chloride solution to decrease as much as three milliliters upon boiling for ten minutes even when great precautions were taken to exclude the air.

English obtained very good results and got by these difficulties by the use of meta- and para-nitroanilines for standards. The problem of decomposition of the titer of titanous chloride on heating was solved by strictly adhering to an established procedure. The same error appeared each time and was corrected for when it appeared in the standard (p-nitroaniline) also. These standards have the distinct advantage in that they are not volatile with steam. It is for this reason that nitrobenzene must be sulfonated in the method of Knecht and Hibbert. m-Nitro-p-toluidine was found satisfactory as a standard, also. (2)

The work of Callan, Henderson, and Stafford is also based on p-nitroaniline as a standard.(3)They worked with both the chloride and the sulfate and recommend the sulfate. However, the sulfate is much more susceptible to oxidation by the atmosphere than the chloride. It is also insoluble in alcohol which may influence some determinations.

(1) C. F. Van Duin, Chem. Weekblad, 16, 1111 (1919)
(2) F. L. English, Ind. Eng. Chem., 12, 994, (1920)
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Callan and Henderson find p-nitroaniline a desirable standard for another reason. A standard solution of it kept around the laboratory can be used for the standardization of such solutions as sodium nitrite, potassium bromate, aniline hydrochloride, etc. From their results using both the titanous chloride and the sulfate, I recommend 3,5,dinitrobenzoic acid as a standard. Theoretical results were obtained by both methods and the fact that no reflux condenser was needed shows that the compound is not volatile with steam.

The work of Hendrixson and Verbeck (1) on the use of permanganate and dichromate in the standardization of titanous sulfate suggested the same for the chloride. Both reactions are satisfactory either directly or thru the medium of ferric iron. The end-point of the dichromate titration is slow and is sometimes lost. The potentiometric method is used in the direct titration. Hendrixson and Verbeck used the method of Knecht and Hibbert and the improved apparatus of Thornton and Chapman. (2) Thornton and Chapman adapted their apparatus from English's improvement of Knecht's. (3)

Jones and Lee used the potentiometric method in the estimation of azo dyes. Ferrous ammonium sulfate oxidized by potassium permanganate was used as a primary standard. (4)

(1) W. Hendrixson and L. Verbeck, J.A.C.S., 44, 2382, (1922)
(2) W. Thornton and J. Chapman, J.A.C.S., 43,91,(1921)
(3) F. L. English, Ind. Eng. Chem., 12, 994, (1920)
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The results of standardization were checked with p-nitroaniline which had been checked against sodium nitrite and were described as agreeing "closely". They show, as did the work of English, that ferrous ammonium sulfate gives a small error as a primary standard. The real disadvantage lies in the instability of the solution. This fault can be overcome, however, by the apparatus of Zintl and Reinäcker (1) whose exponent in this country is G. Frederick Smith of the University of Illinois. Smith has shown ferrous sulfate solutions to be stable when stored under hydrogen in this apparatus.

Kolthoff and Tomicek (2) found the chief impurity in the commercial solutions to be iron as did Knecht. They found it desirable to have iron free material for potentiometric work and they used the method of Polidori mentioned above for purification. They found the preparation of Kahlbaum to be very nearly iron free. That of LaMotte was not as good, but was satisfactory. It cost nearly ten times as much as the Kahlbaum preparation (in Europe). Random commercial samples were not satisfactory.

Satisfactory standardisation of titanous chloride solutions (3) was accomplished electrometrically using pure potassium dichromate, potassium ferricyanide, and ferric alum.

(1) Zintl and Reinäcker, Z. anorg. allgem. Chem., 155, 84, (1926)
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The potassium dichromate was obtained pure by crystallizing the commercial salt from water several times and drying at 180 degrees. Kolthoff has shown that a salt of very high purity can be obtained in this manner. The titration of the titanous solution with dichromate works well except at times the end-point is slow and behaves peculiarly. (1) Potassium ferricyanide was recrystallized repeatedly from water and after air drying, was carefully heated to 100 degrees. Zintl raises the objection to using it as a standard that it is not stable in solution. The results of Kolthoff and Tomicek seem to show slight decomposition. The ferric alum was recrystallized from water rapidly twice and dried over a liquid sugar-sodium chloride mixture whose vapor tension was about 70 %. Solutions of 0.05 M and 0.1 M were prepared by weight. They were in 0.4 N sulfuric acid. The results agreed fairly closely with those of the dichromate. Zintl (2) points out that the salt soon changes its water of hydration appreciably and certainly is too difficult to prepare pure for use in the standardization. In order to get consistent results and an end-point which was satisfactory, Kolthoff and Tomicek introduce a little copper sulfate near the end-point of the titration. This should be corrected for because the cupric copper is reduced to the cuprous state.

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Kolthoff, Tomicek, and Robinson used platinum electrodes and not platinized platinum and were not bothered in their method with a scum collecting on the electrodes as Zintl and Rauch reported in their work. (1) They also used pure copper sulfate for the standardization electrometrically. They reported a low titer and a small break. The trouble was remedied by the addition of a small amount of potassium thiocyanate near the endpoint and nearly theoretical results were obtained. They were not very consistent and the potassium thiocyanate evidently affected the copper solution when dilute near the endpoint. The cuprous salt was probably attacked because the results were approximately 0.1 % high. For the above reasons they do not recommend copper sulfate as a standard. Zintl and Rauch (2) found it quite satisfactory as a standard in their work with metals.

Becker (3) used ferrous ammonium sulfate as a standard. It was oxidized by a hydrochloric acid solution of potassium chlorate, the excess of the oxidizing agent being driven off by two successive evaporations to dryness. This seems to be a much more time consuming method than the oxidation with a dilute solution of potassium permanganate.

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Thornton (2) and Wood standardized titanous sulfate against iron ores. Sibley iron ore was obtained from the Bureau of Standards and proved satisfactory. The iron content was checked by standard potassium dichromate using diphenylamine as indicator and by "cupferon". Values varied over about 30 parts in 1500.

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Anding, Zieber, and Malisoff have used a standard solution of ferric alum as standard. When they estimated nitrobenzene, they used a purified sample of the nitro compound for the primary standard. (1) They worked with titanous sulfate in preference to the chloride. This has been the tendency in all recent work in this country.

Oxalate was the ultimate standard used in the standardization of the titanous chloride which was used in the estimation of quinone in this paper. The method was that of Knecht and Hibbert. The method of English and modifications thereof was used in the other estimations. Results are high if no correction is applied substanciating the evidence that the titanous chloride solution decreases in strength on heating. The iron alum was standardized by reduction with stannous chloride and titration with standard potassium permanganate in some cases and in other cases the reduced solution was oxidized with ceric sulfate solution standardized against sodium oxalate. A standard solution of ceric sulfate in approximately 0.5 N sulfuric acid was found an excellent standard for the standardization of the titanous chloride solution. The titration may be run in either direction. Ferrous o-phenanthroline complex was found to be an excellent indicator. A sharp color change is obtained with 0.02 ml. of 0.05 N solution.

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(2) Contributions to Methods.

The work of Knecht and Hibbert has been extensively reviewed in (A) of this section.

Rhead showed in his estimation of copper by titanous chloride that ammonium chloride, sodium acetate, zinc sulfate, zinc chloride, ferrous sulfate, and stannous chloride do not exert an appreciable influence on titrations with titanous chloride if they are present in reasonable amounts. He varied the amounts of potassium thiocyanate, hydrochloric acid, and sulfuric acid over a wide range and found no effect greater than expected error. He found that a solution as weak as some which Knecht used will precipitate an oxide of titanium when heated to 80 degrees if a great excess of hydrochloric is not present.(1)

In the iron titration with titanous chloride Monnier used sodium tungstate as indicator. The solution is colored blue by the reduction of tungstic acid as soon as an excess of titanous chloride is added. The solution must be weakly acidic and one must work at room temperature. (2) Safranine and induline were also used as indicators.

English used two solutions of different strengths.(3)

(1) Rhead, J.C.S., 89(2), 1491 (1906)
(2) Monnier, Ann. de Chim. anal., 21, 109 (1916)
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(3) F. L. English, Ind. Eng. Chem., 12,994 (1920)

A solution 0.05 N was used for most determinations but one 0.25 N was used for polynitro compounds so that a large sample could be taken. The titanous chloride was boiled with hydrochloric acid, cooled, and then made up to volume. It is necessary to cool the solutions before dilution to prevent the precipitation of oxides or hydrolysis products. 50 ml. of carbon tetrachloride was added to the solution to take up the grease in the distilled water. The apparatus then remained cleaner for a much longer time with this treatment and there appeared to be no change of titre. The ferric alum solution was also treated with carbon tetrachloride.

The method of Knecht was modified by the addition of 25 ml. of 40 % sulfuric acid per final volume of 100 ml. in place of the excess hydrochloric acid. In this solution the time of boiling with the excess titanous chloride was reduced to 5 minutes and tendency to chlorination was reduced. In the back titration the thiocyanate was not added until the color of the titanous solution had been just bleached out with ferric alum. A better end-poimt is obtained using this procedure and there is less effect of the indicator on the titration. As with the method of Knecht and Hibbert (without sulfonation) the mononitro compounds were not completely reduced but the substituted mononitro compounds worked well. When compounds were dissolved in alcohol, it was found that a blank must be run on the same amount of alcohol. (1)

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(1) F. I. English, Ind. Eng. Chem., 13, 994 (1920)

We have seen that Knecht and Hibbert obtained fairly good results in the reduction of alpha-nitronaphthalene only when the amount of hydrochloric acid present was controlled within very narrow limits. Callan, Henderson, and Stafford (1) could not obtain consistent results with the method of Knecht and Hibbert by acid control alone. They had trouble from chlorination, they believed. A solution of the organic compound in alcohol seemed to increase chlorination. Therefore they suggested the use of the sulfate in order to get around these difficulties. Using the sulfate, good results were obtained with alpha-nitronaphthalene, o-nitroanisole, and nitrocresylmethyl ether. All three had not been successfully reduced with the chloride. The only disadvantage encountered with the sulfate was that it is more sensitive to oxidation in the air.

Callan and Henderson (2) checked the work of English with both the chloride and the sulfate. Certain compounds which were volatile with steam and also difficult to reduce were found resistant to the sulfate also. The fact was, the compound volatilized before the reducing agent had attacked it completely. These compounds, the principle ones were nitrobenzene and alpha-nitronaphthalene, were successfully

(1) T. Callan, J. Henderson, and N. Stafford, J. S. C. I., 39 (1), 86 (1920)
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(1) T. Gallan, J. Henderson, and N. Stafford, J. S. C. I., 39 (1) 86 (1920)
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estimated when the reduction was carried out under a small 9 inch reflux condenser which was connected to the flask by a ground glass connection. The amount of titanous solution was found to be of minor importance as long as a reasonable excess (25 ml. of 0.05N solution for each 100 ml. of final solution-English) was present. But the amount of hydrochloric acid was found to be of great importance. p-Nitroanisole gave 97 % reduction using the minimum amount of hydrochloric acid and only 85 % when four times that amount of acid was used. These results were obtained by the method of English. Using titanous sulfate 99.7 % and 99.8% were found. Therefore, the sulfate is superior to the chloride for some types of organic compounds. An approximately 5% solution of the sulfate is recommended.

In their estimation of nitroparaffins T. H. Henderson and A. Macbeth (1) added 10 ml. of an alcoholic solution of the nitroparaffin to a solution containing excess of titanous chloride and boiled gently under the reflux condenser for a half hour. The solution was then made up to 500 ml. and aliquot portions titrated with iron alum. This final step is difficult to perform without loss from oxidation of the solution in air. The reductions were roughly quantitative for mono-, di-,and tri-chloro- and -bromo compounds. The trinitroparaffins reacted as expected, requiring eighteen

T. Henderson and A. Macbeth, J.C.S., 121(1), 892, (1922)

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In their estimation of nitroperelins T. H. Henderson and A. Meebeth (I) added 10 ml. of an alcoholic solution of the nitroperelin to a solution containing excess of titanous chloride and boiled gently under the reflux condenser for a half hour. The solution was then made up to 500 ml. and aliquot portions titrated with iron alum. This final step is difficult to perform without loss from oxidation of the solution in air. The reductions were roughly quantitative for mono-, di-,and tri-chloro- and -bromo compounds. The trinitroperelins reacted as expected requiring eighteen

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equivalents of titanous chloride for complete reduction. Guanidine was the reduction product. The equation for the reaction with the trinitrochloromethane is as follows:

$ClC(NO_2)_3$ plus 9 H_2 equals $(NH_2)_2C{:}NH$ plus HCl plus 6 HOH

The tetranitro compound did not behave as expected. In that case the product was also guanidine:

$C(NO_2)_4$ plus 18 H equals $(NH_2)_2C{:}NH$ plus HNO_2 plus 6 HOH

The first reduction in the case of the tetranitro compound is the removal of the labile nitro group. Then the reduction proceeds as in the trinitro compound. The purpose of the paper was to show the labile nature of the halogen atom in organic compounds. A labile nitrogen was found also. A list of the compounds reduced follows in Table I, II, C. (p. 38)

Jones and Lee (1) estimated azo dyes by the method of English except that after reduction with excess titanous chloride, the end-point of the back titration with ferric alum was found potentiometrically.

Calcott and English (2) estimated 30 representative dyes of the triphenylmethane and azo series with an average error of about 0.5 %. They showed that the deep colors and the troublesome precipitates encountered in the usual procedures could be prevented by judicious choice of solvent,

(1) Jones and Lee, Ind. Eng. Chem., 14, 46 (1922)
(2) Calcott and English, Ind. Eng. Chem., 15, 1042 (1923)

and then the end-point was made much clearer. Knecht (1) had found it necessary to add alcohol to clear up the solution and get a satisfactory end-point in the titration of Eosin A. Calcott and English (2) found that the sodium tartrate or the Rochelle salt should never be boiled with the solution when the titanous chloride was present because the titanous chloride was oxidized by the free acid formed. Knecht did not believe that it had any affect.

Callan and Stafford (3) have used an ingenious method for the analysis of the aryl-guanidines. Their method will certainly be further applied to compounds which are difficult to estimate . It is based on the comparative ease with which the nitro groups in picric acid may be reduced with titanous chloride. The picrate salt was made and then a known weight of the pure salt was estimated in the usual manner with titanous chloride.

Zintl and Rauch have shown that tartaric acid added to the solution in titrating a weakly acid or an alkaline solution of titanous chloride prevents the precipitation of the oxide.(4)

(1) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" Second edition (1925) p. 106.
(2) W. S. Calcott and F. L. English, Ind. Eng. Chem., 15, 1042 (1923)
(3) T. Callan and N. Stafford, J. S. C. I., 43 (part I), 1T (1924)
(4) E. Zintl and A. Rauch, Z. Elektrochem., 31, 428 (1925)

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(1) E. Knecht and M. Hibbert, "New Reduction Methods in Volumetric Analysis" Second edition (1925) p. 186.
(2) W. S. Calcott and F. I. English,
Ind. Eng. Chem., 15, 1042 (1923)
(3) T. Callan and W. Stafford,
J. S. C. I., 43 (part I), 17 (1924)
(4) E. Zinzi and A. Rauch,
Z. Elektrochem., 31, 458 (1925)

We have seen above that Van Duin, Rhead, and others have shown that the titer of titanous chloride decreases on heating. Van Duin, and later English have shown that blanks must be run which are treated the same way in detail as the estimations, whether the chloride or the sulfate be used. From the measurement of reduction potentials in the sulfate solution, Diethelm and Foerster conclude that the titanous (1) ion may discharge the hydrogen ion with the evolution of hydrogen gas at boiling temperature. Heating is required for reduction of most types of organic compounds by the methods given. Kolthoff had shown that the reducing action of titanous chloride was inversely proportional to the concentration of the hydrogen ion. (2) Therefore, Kolthoff and Robinson tried titanous chloride reductions at low hydrogen ion concentrations and at room temperature. Sodium carbonate and sodium acetate were added to the solution to buffer it and decrease the hydrogen ion content. They were not satisfactory because titanous and titanic hydroxides were precipitated. Rochelle salt was tried but a precipitate was usually obtained. Sodium citrate was found to be satisfactory. In the presence of this salt nitro groups were found to be reduced rapidly at room temperature. Three minutes in contact with the titanous chloride was sufficient. The solution was then acidified again and the back titration performed with irom alum using potassium

(1) Diethelm and Foerster, Z. physik. Chem.,63, 138(1908)
(2) Kolthoff, Rec. trav.chim., 43, 268 (1924)

thiocyanate as indicator. Titrations performed at 50 degrees were just as successful as those at room temperature. A slight correction was applied for the influence of the sodium citrate on the titration. This correction was obtained from a blank run under the same conditions.

Dachselt titrated nitro and nitroso compounds potentiometrically using the direct method at temperatures from 50 to 80 degrees. He states that the presence of Rochelle salt was desirable, but good breaks on the curves could be obtained if slow titrations were carried out without the salt. His results were in error from 0.07 % to 0.72 % from the theoretical. (1) The color end-point seemed to appear after the potentiometric end-point. The apparent decrease in strength of titanous salts may be more complicated than to be just explained to be due to decomposition on heating.

Wilkinson and Tyler (2) found that malachite green behaved normally with titanous sulfate when 50 ml. of the saturated solution was present in each 150 ml. of final solution. Results checked with the chloride using the method of Knecht. They (3) showed that titanous sulfate could be kept in a burette for 19 hours without appreciably changing concentration. Decomposition was rapid after that. Stored under naphtha

(1) E. Dachselt, Z. anal. Chem., 68, 405 (1926)
(2) Wilkinson and Tyler, J. S. D. and C.,43, 116 (1927)
(3) Wilkinson and Tyler, J. S. D. C., 43, 114 (1927)

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over zinc amalgam, the solution decreased in strength about .27 % in 21 hours. Using an alkaline solution of pyrogallol in absorption tubes connected to the opening of the storage bottle to rid the entering air of oxygen, the solution was found to decrease in strength about 0.5 % in three days and 2.2 % in fourteen days.

Becker has obtained practically theoretical results for nitroglycerol and ethyleneglycol dinitrate (1) by dissolving the sample in acetic acid, adding an excess of ferrous chloride, hydrochloric acid, boiling, and then titrating the resulting ferric iron with a standard solution of titanous chloride which had been standardized against ferrous ammonium sulfate oxidized by potassium chlorate. Ammonium thiocyanate was used as indicator. When present in the mixture, 2,4-dinitrotoluene does not interfere and may be accurately determined using excess titanous chloride in the usual method for nitrocompounds. Diethyldiphenylurea or diphenylamine, when present in small amount, does not interfere.

(1) W. W. Becker, Ind. Eng. Chem., Anal. Ed., 5, 152, (1933)

over zinc amalgam, the solution decreased in strength about .27 % in 21 hours. Using an alkaline solution of pyrogallol in absorption tubes connected to the opening of the storage bottle to rid the entering air of oxygen, the solution was found to decrease in strength about 0.8 % in three days and 2.2 % in fourteen days.

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3. Reactions not Quantitative.

It was mentioned above in the work of Knecht and Hibbert that various organic acids are slowly acted upon by titanous chloride solution. Monnier (1) has used neutral and basic solutions of titanous chloride for the identification of organic acids. Characteristic colored precipitates and solutions serve to distinguish several different acids. The compounds, however are not described except from a physical point of view. For instance, benzoic acid gives a deep green-brown precipitate. Acetic acid was shown to form precipitates with titanous chloride similar to those with iron and aluminum. Upon boiling basic salts were precipitated very similar to those formed from iron salts.

In the review of Knecht's work alpha-nitronaphthalene was shown to react with a great excess of acid titanous chloride to form mainly 4-chloro-alpha-naphthylamine.

Wieland (2) and Kloss prepared the corresponding hydrocarbon from phenylethinyldiphenyl carbinol. They used the following method:

Treat three grams of the carbinol in 25 ml. of alcohol with 2 N titanous chloride solution until the color remains purple even after warming to 60 degrees for a few minutes. Extract with ether, shake with water, separate, dry with

(1) M. A. Monnier, Ann. chim. anal., 20, 1 (1915)
(2) H. Wieland and H. Kloss, Ann., 470, 217 (1929)

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sodium sulfate, and evaporate on a water bath. The product crystallizes from the alcohol concentrate in needles. The hydrocarbon gives a melting point of 174 degrees when recrystallized from an acetic acid-alcohol mixture.

Sweet and Marvel (1) prepared the corresponding hydrocarbon from diphenyl-tert.-butylethinyl carbinol by allowing a titanous chloride solution to drop on the carbinol in a three-neck flask fitted with a stirrer and a reflux condenser. The yield was about 25 % of the hydrocarbon with melting point 150-151 degrees. In another experiment 10 grams of the carbinol gave 1.5 grams of the hydrocarbon and 8 grams of 1,1-diphenyl-4,4-dimethylpentene-1-one-3 with melting point 65-66 degrees. Three grams of 3-methyl-3-ethylpentinyl-1)-diphenyl carbinol treated similarly gave 1.29 grams (44 %) of the hydrocarbon with melting point 105-106 degrees,and 3 grams of tri-tert.-butylethinyl carbinol gave 0.314 grams of the hydrocarbon $C_{38}H_{54}$ with melting point 171-172 degrees.

The influence of an ammoniacal solution of titanous chloride on certain double bond linkages was shown by the work of Karrer, Yen, and Reichstein. (2) PhCH:CHPh, PhPhC:CHH, and PhC ⋮ CPh resisted reduction whereas PhCH:CHCOOH,

(1) R. Sweet and C. Marvel, J. A. C. S., 54, 1184-1190 (1932)

(2) P. Karrer, Y. Yen, and I. Reichstein, Helv. chim. acta., 13, 1308-1319 (1930)

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PhCH:CHCONH$_2$, and PhCH:CHAc were transformed to the respective saturated compounds. PhCH:CHCH:CHCOOH gave principally PhCH$_2$CH:CHCH$_2$COOH and a smaller yield of PhCH:CHCH$_2$CH$_2$COOH. PhCH:CHCOOC$_2$H$_5$ and PrCH:CHCOOH would not reduce. It appears that only a linkage of double bond next to the carbonyl group is reduced by titanous chloride in ammonia. Flavones were reduced to pinacols and flavans. Quercetimlpentamethyl ether gave pentamethylcyanidin. Benzalacetone was reduced to benzylacetone and the product identified by boiling point and the semicarbazone derivative.

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C. Table I. Organic Compounds Quantitatively Reduced by Titanous Chloride

(Only representative dyes are included)

Knecht and Hibbert:

Alizarin
Alizarin S
Anthraquinone
Benzene Diazonium Chloride
Benzopurpurin 4 B
Benzoquinone
Brilliant Yellow
Chrysophenine
Cotton Scarlet
Crystal Scarlet 6 R
Crystal Violet
m-Dinitrobenzene
Dinitrostilbene Disulfonic Acid
Dinitrotoluene
Eosin
Gallein
Indigo
Isatin
Malachite Green
Methylene Blue
o-Naphthoquinone
p-Nitroaniline
Nitrobenzene and Nitrotoluene (sulfonated)
p-Nitrosodimethylaniline
p-Nitrosophenol
Picric Acid
Pararosaniline Hydrochloride
Pararosanilinetrisulfonic Acid
Phenolphthalein
Phenylazo-beta-naphthol
Phenylglucosazone
Phenylhydrazine (oxidized with methylene blue)
Tetramethyldiaminobenzhydrol
Toluquinone
Tolusafranine
sym-Trinitrocresol
sym-Trinitrotoluene
sym-Trinitroxylenol

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Chrysophenine
Cotton Scarlet
Crystal Scarlet 6 R
Crystal Violet
m-Dinitrobenzene
Dinitrosostilbene Disulfonic Acid
Dinitrotoluene
Eosin
Gallein
Indigo
Isatin
Malachite Green
Methylene Blue
o-Naphthoquinone
p-Nitraniline
Nitrobenzene and Nitrotoluene (sulfonated)
p-Nitrosodimethylaniline
p-Nitrosophenol
Picric Acid
Pararosaniline Hydrochloride
Pararosanilinetrisulfonic Acid
Phenolphthalein
Phenylene-beta-naphthol
Phenylglucosazone
Phenylhydrazine (oxidized with methylene blue)
Tetramethyldiaminobenzhydrol
Toluquinone
Toluazfrazine
sym-Trinitrocresol
sym-Trinitrotoluene
sym-Trinitroxylenol

Table I. Organic Compounds Reduced Quantitatively

by Titanous Chloride (con.)

Robinson, F. :

p-Nitrophenylhydrazine
p-Nitrophenylhydrazone (1)

Willson:

2,4-Dinitrophenylhydrazine

Embleton:

Benzil

Van Duin:

Aminonitrophenylmethylnitramine
m-Dinitrobenzol
Hexanitrodiphenyl Sulfide
Hexanitrodiphenyl Sulfone
Tetranitroaniline
Tetranitrophenol
Tetranitrophenylmethylnitramine (low)
Trinitrodimethyldinitraminobenzol
Trinitromethylnitraminoanisol
Trinitromethylnitraminophenol
sym-Trinitrophenylmethylnitramine

Atack:

beta-benzildioxime
benzophenoneoxime

Henderson and Macbeth: (rough quantitative)

Nitromethane
Bromdinitromethane
Bromtrinitromethane
Chlorotrinitromethane
Dibromdinitromethane
Picryl Chloride
Tetranitromethane
Trinitromethane

(1) F. Robinson, J. S. D. and C., 32, 80 (1916)

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Embleton:

Benzil

Van Dam:

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m-Dinitrobenzol
Hexanitrodiphenyl Sulfide
Hexanitrodiphenyl Sulfone
Tetranitroaniline
Tetranitrophenol
Tetranitrophenylmethylnitramine (low)
Trinitrodimethylnitraminobenzol
Trinitromethylnitraminoanisol
Trinitromethylnitraminophenol
sym-Trinitrophenylmethylnitramine

Atack:

beta-benzildioxime
benzophenoneoxime

Henderson and Macbeth: (rough quantitative)

Nitromethane
Bromdinitromethane
Bromtrinitromethane
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Picryl Chloride
Tetranitromethane
Trinitromethane

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Table I. Organic Compounds Reduced Quantitatively by Titanous Chloride (con.)

English: (original and those of improved method)

m-Dinitrobenzene
Dinitrochlorobenzene
Dinitrodichlorobenzene
Dinitrodichlorotoluene
Dinitrotoluene
m-Nitroaniline
p-Nitroaniline (standard)
p-Nitrobenzylchloride
Nitrochlorobenzenesulfonic Acid
o-Nitrophenol
p-Nitrophenol
m-Nitro-p-toluidine
o-Nitro-p-toluidine
Picramic acid
Trinitrobenzene
Trinitroxylene

Callan, Henderson, and Stafford: (chloride and sulfate)

3,5-Dinitrobenzoic Acid (100.0%)
1,2,4-Dinitrophenol
o-Nitroanisole
Nitrobenzene (without sulfonation)
o-Nitrobenzoic Acid
p-Nitrobenzoic Acid
m-Nitrobenzoic Acid
Nitrocresylmethyl Ether
o-Nitro-p-cresol
alpha-Nitronaphthalene
3-Nitrophthalic Acid
Nitrotoluene
Nitroxylene
Sodium-p-nitrochlorobenzenesulfonate
Trinitro-m-cresol

Table I. Organic Compounds Reduced Quantitatively

by Titanous Chloride (cont.)

English: (original and those of improved method)

m-Dinitrobenzene
Dinitrochlorobenzene
Dinitrodichlorobenzene
Dinitrodichlorotoluene
Dinitrotoluene
m-Nitroaniline
p-Nitroaniline (standard)
p-Nitrobenzylchloride
Nitrochlorobenzenesulfonic Acid
o-Nitrophenol
p-Nitrophenol
m-Nitro-p-toluidine
o-Nitro-p-toluidine
Picramic acid
Trinitrobenzene
Trinitroxylene

Callan, Henderson, and Stafford: (chloride and sulfate)

3,5-Dinitrobenzoic Acid (100.0%)
1,3,4-Dinitrophenol
o-Nitroaniline
Nitrobenzene (without sulfonation)
o-Nitrobenzoic Acid
p-Nitrobenzoic Acid
m-Nitrobenzoic Acid
Nitrocresylmethyl Ether
o-Nitro-p-cresol
alpha-Nitronaphthalene
3-Nitrophthalic Acid
Nitrotoluene
Nitroxylene
Sodium-p-nitrochlorobenzenesulfonate
Trinitro-m-cresol

Table I. Organic Compounds Reduced Quantitatively by Titanous Chloride (con.)

Callan and Stafford:

alpha-Nitroso-beta-naphthol

The Picrate Salts ofRubber Vulcanization Accelerators:

Diphenylguanidine
Di-p-tolylguanidine
o-Tolylguanidine
Tolylphenylguanidine
Triphenylguanidine
Tritolylguanidine

Becker:

Ethyleneglycol Dinitrate
Nitroglycerol

III. APPARATUS

Knecht stored the titanous chloride solution in an aspirator bottle supported about four feet above the work table. The side outlet was fitted with a rubber stopper through which glass tubing passes. This tubing is connected to the T-tube which forms the lower portion of the burette and which holds the bead valve and burette tip. (Figure I) A two-hole stopperis fitted in the top of the bottle. Glass tubing is fitted in both holes flush with the inside of the stopper. One tube leads to the top of the burette and is connected to it by means of a rubber stopper. This tube serves to allow the passage of gas back into the bottle when the solution is allowed to run into the burette. When the burette is filled, a bead valve in the line from the bottom cork to the bottom of the burette is opened to allow the solution to run. It stops the flow by closing automatically when the pressure of the fingers is released. The other tube from the top of the bottle leads to the hydrogen supply. For this Knecht used a glass cylinder half filled with a mixture of equal parts of hydrochloric acid and water, into which dipped an inner tube contracted at the bottom to a narrow aperture, and fitted at the top with a rubber stopper with a hole to receive the tube which led into the storage bottle. The inner tube contained granulated zinc which was attacked by the acid as soon as the bead valve on the burette was opened.

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The air is expelled from the apparatus by opening the valve in the storage line and allowing the liquid to fill the burette and the tube above it as far as possible. This liquid is then drawn off by opening the bead valve on the burette. This valve is kept open for some time so that the hydrogen running through the system will flush it and remove the air. Then the burette valve is closed and the supply valve opened to fill the burette. The system is then ready for use. (1) A 1% solution of hydrofluoric acid is used to remove deposits when cleaning the storage bottle. Rubber stoppers are cleaned and softened by wiping with a cloth soaked in toluene. Carbon dioxide is furnished by a small test-tube generator similar to the hydrogen generator, but was not generally used in the back titration.

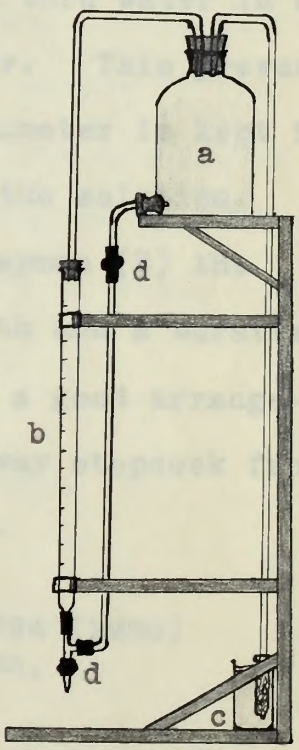

Figure I.

(a) Storage bottle.

(b) Burette.

(c) Hydrogen generator.

(d) Bead valves.

(1) Knecht and Hibbert, "New Reduction Methods...", p.63.

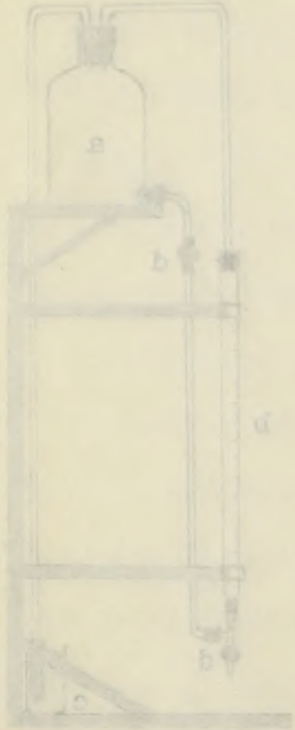

Figure 1.

(a) Storage bottle.

(b) Burette.

(c) Hydrogen generator.

(d) Seed valves.

English (1) uses a Kipp generator for the source of the hydrogen over the solution. The hydrogen is bubbled thru concentrated titanous chloride solution to remove impurities. Regular glass stopcocks are used in place of bead valves because they are more accurate and dependable especially under pressure. Considerable adsorbed and enclosed air can be shown to be in marble. Therefore English recommends the use of pink Tennessee marble in the Kipp generator because it was shown that it has much less enclosed air than the Vermont variety. Carbon dioxide is kept flowing over the solution during the whole course of the estimation. A 300-ml. Erlenmeyer flask fitted with a three-hole rubber stopper serves for the titration chamber. The carbon dioxide enters one hole, leaves the other, and the burette point fits into the third hole. The carbon dioxide is run thru water in a small flask on leaving the titration chamber. This prevents back diffusion of air on cooling. A thermometer is kept in the siphon tube to show the temperature of the solution.

In the apparatus of Thornton and Chapman (2) the stopcock in the supply line is dispensed with and a burette used with a two-way stopcock. This is not a good arrangement because it is difficult to keep a two-way stopcock from leaking under the pressure of the generator.

(1) English, Ind. Eng. Chem., 12, 994 (1920)
(2) W. M. Thornton and J. E. Chapman,
J. A. C. S., 43, 91, (1921)

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Callan and Henderson (1) introduced the use of the reflux condenser for compounds not easily reduced which are volatile with steam. A small nine inch condenser was fitted to the titration flask when the solution was heated during reduction. Aground glass joint was used. The carbondioxide was run into the solution thru the condenser by means of a thin glass tube. A three-hole glass stopper was ground to fit the titration flask and was used in the titration proper. Hendrixson and Verbeck (2) introduce electrodes in the carbon dioxide openings and use an extra opening for a stirring device in their electrometric standardization of the sulfate. Zintl and Rauch (3) do not connect the top of the burette with the space in the storage bottle but protect it with a Bunsen valve. Kolthoff and Robinson (4) free the carbon dioxide of oxygen by running it through a wash bottle containing a 5 % solution of titanous chloride and sodium citrate enough in the solution to make it 20 %. Zintl criticized Kolthoff for his use of the saturated solution of the titanous chloride alone for this purpose in Kolthoff's previous work.

(1) T. Callan and J. A. Henderson,
J. S. C. I., 41 (part I), 157 T (1922)
(2) W. S. Hendrixson and L. M. Verbeck,
J. A. C. S., 44, 2382 (1922)
(3) E. Zintl and A. Rauch,
Z. Elektrochem., 31, 428 (1925)
(4) I. M. Kolthoff and Conmar Robinson,
Rec. trav. chim., 45, 169 (1926)

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Z. Elektrochem., 31, 428 (1925)
(4) I. M. Kolthoff and Conner Robinson,
Rec. trav. chim., 45, 189 (1926)

Wilkinson and Tyler (1) stored the solution of titanous sulfate over zinc amalgam under naphtha. The burette was sometimes left open to the air. They (2) also tried using an alkaline solution of pyrogallol in absorption tubes connected to the mouth of the storage bottle to remove the oxygen from the entering air. Becker (3) , in a recent article, states that he uses carbon dioxide in the storage bottle as well as for protection in the titration. He uses a special Florence-type 300-ml. flask which has a small inlet tube for the carbon dioxide sealed in on the shoulder. A small condenser is fitted to the flask with a ground glass joint. In the titration the flask is fitted with a one-hole rubber stopper through which is inserted a short piece of 8mm. glass tubing which takes the burette tip and allows the exit of the carbon dioxide. Anding, Zieber, and Malisoff (4) use a similar set-up. They use a stirrer whose shaft extends all the way through the opening in the condenser. With this arrangement they can titrate hot without loss and the chamber need not be opened to air during the titration except at the top of the condenser.

(1) Wilkinson and Tyler,
J. S. D. and C., 43, 114 (1927)
(2) Wilkinson and Tyler,
J. S. D. and C. , 43, 225 (1927)
(3) W. W. Becker,
Ind. Eng. Chem., Anal. Ed., 5, 152-154 (1933)
(4) C. E. Anding, Jr., B. Zieber, and W. M. Malisoff,
Ind. Eng. Chem., Anal. Ed., 6, 41 (1934)

IV. METHODS FOR THE PREPARATION AND USE OF TITANOUS CHLORIDE

A. Method of Knecht and Hibbert. (1)

1. Preparation of Solution.

Fifty milliliters (50 ml.) of the commercial 20 % solution of titanous chloride are boiled for one minute with 100 ml. of concentrated hydrochloric acid in a small flask. The mixture is then cooled and made up to 2¼ liters in the storage bottle. The solution should occupy the entire capacity of the bottle so that the air can readily be replaced above the solution by the hydrogen.

The iron alum solution for the back titrations is prepared in dilute sulfuric acid with a concentration of 14 g. per liter. The solution is filtered if basic salts precipitate. Sulfuric acid is added then, until the solution becomes a pale straw color. These solutions run approximately 0.03 N.

2. Procedures.

Nitro Compounds (picric acid) (2)

One gram of picric acid is dissolved in 1 liter of water. 10 ml. of this solution is acidified with hydrochloric acid, and 50 ml. of standard titanous chloride solution are added. The solution is boiled for ten minutes, and then cooled to room temperature or below. Carbon dioxide is kept

(1) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" Second Edition. (1925) Longman's, Green, and Co. p. 62.

(2) E. Knecht and E. Hibbert, ibid., p. 92.

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(1) R. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" Second Edition. (1925) Longman's, Green and Co. p. 82.

(2) R. Knecht and E. Hibbert, ibid., p. 92.

flowing through the flask throughout the reduction. It is not used ordinarily in the back titration. 10 ml. of ammonium thiocyanate are then added and then iron alum added to the red color permanent for at least 15 seconds. Here is the equation:

$C_6H_2(OH)(NO_2)_3$ plus 18 HCl plus 18 $TiCl_3$ equals

$C_6H_2(OH)(NH_2)_3$ plus 6 HOH plus 18 $TiCl_4$

The equivalent iron value of the titanous chloride is found by running a blank. The amount of nitro compound is computed in terms of iron.

Nitroso Compounds (Direct method) (1)

One gram of p-nitrosodimethylaniline is dissolved in hydrochloric acid and made up to ¼ l. with water. 50 ml. of this solution are warmed over a Bunsen to 40-50 degrees, carbon dioxide passed into the flask, and the solution then titrated with titanous chloride until the yellow color is completely destroyed. Methylene blue may be used for indicator and is preferred when quinone is estimated by the direct method.

Equation:

$C_6H_4N(CH_3)_2NO$ plus 4 HCl plus 4 $TiCl_3$ equals

$C_6H_4N(CH_3)_2NH_2$ plus HOH plus 4 $TiCl_4$

The nitroso compound is calculated in terms of iron from the known iron value of the titanous chloride.

(1) E. Knecht and E. Hibbert, "New Reductions Methods in Volumetric Analysis" Second edition. (1925) p. 95-96. Longmans, Green, and Company, London.

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(1) E. Kneebt and E. Hibbert, "New Reductions Methods in Volumetric Analysis" Second edition. (1925) p. 85-98. Longmans, Green, and Company, London.

B. Method of English. (1)

1. Preparation of Solutions.

All water used in the determinations and in solutions for them is boiled for 20-30 minutes and then cooled in an atmosphere of carbon dioxide. This treatment assures nearly oxygen free water.

Two strengths of titanous chloride solutions are prepared. To prepare the 0.05 N solution, for each liter of solution desired, 33.5 ml. of 20 % solution of titanous chloride and 70 ml. of concentrated hydrochloric acid are boiled for 1 minute and then cooled in an atmosphere of carbon dioxide. This solution is added to the water in the container with stirring and all the time running carbon dioxide through it. The 0.25 N. solution of titanous chloride is prepared in a similar manner using 167 ml. of the 20 % solution and 150 ml. of concentrated hydrochloric acid. If any sediment forms, it is filtered off immediately. 50 ml. of carbon tetrachloride are added to the solution in the stock bottle to absorb the grease in the solution and hence keep the apparatus cleaner for a longer time.

The ferric alum solution contains 24.2 g. of ferric alum and 50 ml. of 40 % sulfuric acid per liter. It is treated with carbon tetrachloride also. All of the iron is oxidized to the ferric state by the addition of potassium permanganate

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(1) English, Ind. Eng. Chem., 12, 994 (1920)

until a very faint pink color is perceived.

A solution of 40 % sulfuric acid in oxygen free water is prepared for use in the titrations. Sulfuric acid helps prevent chlorination.

2. Procedure.

English (1) developed his method for the estimation of the nitro group in organic compounds. A sample containing 0.02 to 0.025 g. of nitro nitrogen is weighed accurately. The sample is then dissolved in water, alcohol, or acetic acid. Warming may be necessary. The solution is diluted to 500 ml. and 25 ml. of this solution is then transferred to the 300-ml. Erlenmeyer-type titration flask.

Then 25 ml. of 40 % sulfuric acid are added, the flask connected to the titanous chloride burette, and a current of carbon dioxide allowed to flow through it for five minutes to displace all of the air. 50 ml. of standard titanous chloride are added, the flask removed from the burette, and the hole plugged with a glass rod. The contents are maintained just at boiling for five minutes and the rate of flow of the carbon dioxide is decreased. The rate of flow of the carbon dioxide is then increased again and the flask cooled in cold water. If the volume of the solution has decreased appreciably, distilled water is added with a pipette through the hole in the rubber stopper. The flask is then connected to the iron

(1) F. L. English, Ind. Eng. Chem., 12, 994 (1920)

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(1) J. I. English, Ind. Eng. Chem., 12, 994 (1920)

alum burette and iron alum added until the violet color of the titanous chloride solution just fades out. Then 10 ml. of 10 % ammonium thiocyanate solution are added through the stopper by means of a pipette. The flask is again connected to the iron alum burette and the solution added to a faint red color permanent for one minute. The amount of titanous chloride excess after boiling should never be less than 25 ml. of 0.05 N solution in a volume of 100 ml.

The method (1) differs from that of Knecht and Hibbert in that:

(1) Sulfuric acid is substituted for hydrochloric acid because it was found that there was less reduction of solution by the titanous chloride and less apparent chlorination.

(2) The period of boiling (better keeping at the boil) is reduced to 5 minutes.

(3) The loss of solution in boiling is replaced.

(4) Ammonium thiocyanate is added toward the end of the titration as ferric chloride reacts slightly with it.

Callan and Henderson prefer to use the sulfate in place of the chloride for the first and fourth reasons.

Jones and Lee (2) applied the method of English to the determination of azo dyes obtaining the end-point electrometrically.

(1) F. L. English, Ind. Eng. Chem., 12, 994 (1920)
(2) Jones and Lee, Ind. Eng. Chem., 14, 46 (1922)

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(1) W. E. English, Ind. Eng. Chem., 12, 904 (1920)
(2) Jones and Lee, Ind. Eng. Chem., 14, 46 (1922)

Soon after this work Calcott and English (1) applied the method of English to the determination of the azo dyes and the dyes of the triphenylmethane series using the ammonium thiocyanate indicator, not varying the method except in choice of solvents which was necessary in order to get distinct end-points. They used Rochelle salt or sodium tartrate in direct titrations but not in the indirect titrations in which iron alum was used. Dachselt (2) titrated nitro and nitroso compounds directly at 50-80 degrees and found that though he could obtain usable results without Rochelle salt, the titration was speeded up and was much more satisfactory using the salt. The work of Kolthoff and Tomicek was covered in the part of this paper on standardizations. (p. 20-22)

C. Method of Kolthoff and Robinson. (3)

1. Preparation of Solutions.

The titanous chloride and iron alum solutions are prepared according to the method of English. A quantity of 20 % sodium citrate solution is prepared. A 20 % sodium citrate solution containing 5 % titanous chloride is prepared for use in the wash bottle to rid the carbon dioxide of oxygen.

2. Procedure.

The direct titration at 60 degrees required 40-50

(1) W. S. Calcott and F. L. English, Ind. Eng. Chem., 15, 1042 (1923)
(2) Ernst Dachselt, Z. anal. Chem., 68, 405 (1926)
(3) I. M. Kolthoff and Conmar Robinson, Rec. trav. chim., 45, 169 (1926)

minutes. Therefore the back titration method with iron alum was used. The indirect method with iron alum worked just as well at 50 degrees as at room temperature.

In the titration 25 ml. of the solution of the nitro compound are placed in the titration beaker. 30 ml. of 20 % sodium citrate and a little hydrochloric acid are added. 0.25 g. of sodium bicarbonate is added to rid the solution of dissolved oxygen. Carbon dioxide is allowed to flow through the beaker for three minutes to drive out the air, and the stream is continued throughout the titration. Standard titanous chloride solution is run in slowly until the color of the solution is intense violet showing the presence of an excess of from 1 to 3 ml. The color is much deeper than usual in the presence of the citrate. After 2 or 3 minutes standing at room temperature, the back titration with iron alum is begun. The end-point is determined electrometrically. If desired, equally as good resultsmay be obtained by adding 20 ml. of concentrated hydrochloric acid to the solution before the beginning of the back titration, and 5 ml. of 10 % KCNS solution when near the end-point. Using the potassium thiocyanate end-point, the results were 2 parts in a thousand lower on the average than those for the potentiometric end-point.

Bubbling the carbon dioxide through the titration solution was tried as a means of keeping the solution better isolated from the air but was abandoned when it was found that several compounds were volatile in the flowing gas.

D. The Method of Becker. (1)

1. Preparation of the Solutions.

A 0.2 N titanous chloride solution is prepared according to the directions of English. (See IV-B-1 of this paper) For each liter of solution desired, 150 ml. of 20 % titanous chloride and 100 ml. of concentrated hydrochloric acid are required. A 0.7 N ferrous chloride solution is used. For each liter of solution required, 200 g. of ferrous chloride ($FeCl_2 \cdot 4HOH$) and 50 ml. of concentrated hydrochloric acid are used. An approximately 0.15 N solution of ferric alum is prepared by dissolving 75 g. of ferric alum in 25 ml. of 95 % sulfuric acid with the slow addition of water. The solution is then made up to a liter.

2. Method for the Determination of Nitroglycerol, or 2,4-Dinitrotoluene and Nitroglycerol in Admixture.

Dissolve the weighed sample in acetic acid and make up to volume in a 250-ml. volumetric flask. Transfer a 25-ml. aliquot portion to the special titration flask. Sweep out the air by running through it a stream of carbon dioxide for 5 minutes. Add 15 ml. of ferrous chloride solution and then 25 ml. of hydrochloric acid (1 to 1), connect the flask to the reflux condenser, and then boil for five minutes. Add a few glass beads to prevent bumping.

Increase the current of carbon dioxide, then immerse the

(1) W. W. Becker, Ind. Eng.Chem., Anal. Ed.,5,152(1933)

D. The Method of Becker. (1)

1. Preparation of the Solutions.

A 0.2 N titanous chloride solution is prepared according to the directions of Knöllich. (See IV-B-1 of this paper) For each liter of solution desired, 130 ml. of 20 % titanous chloride and 100 ml. of concentrated hydrochloric acid are required. A 0.7 N ferrous chloride solution is used. For each liter of solution required, 200 g. of ferrous chloride ($FeCl_2 \cdot 4H_2O$) and 50 ml. of concentrated hydrochloric acid are used. An approximately 0.15 N solution of ferric alum is prepared by dissolving 75 g. of ferric alum in 25 ml. of 95 % sulfuric acid with the slow addition of water. The solution is then made up to a liter.

2. Method for the Determination of Nitroglycerol, or 2,4-Dinitrotoluene and Nitroglycerol in Admixture.

Dissolve the weighed sample in acetic acid and make up to volume in a 250-ml. volumetric flask. Transfer a 25-ml. aliquot portion to the special titration flask. Sweep out the air by running through it a stream of carbon dioxide for 5 minutes. Add 15 ml. of ferrous chloride solution and then 25 ml. of hydrochloric acid (1 to 1), connect the flask to the reflux condenser, and then boil for five minutes. Add a few glass beads to prevent bumping.

Increase the current of carbon dioxide, then immerse the

(1) W. W. Becker, Ind. Eng.Chem., Anal. Ed.,5,152(1933)

flask in a bath of cold water and cool, keeping the index finger over the top of the condenser until the hot vapors have all condensed. After cooling to room temperature, disconnect the condenser, insert the one-hole stopper, and titrate with titanous chloride solution until near the end-point. Add 5 ml. of 20 % ammonium thiocyanate solution and titrate until the red color of the ferric thiocyanate just disappears.

Determine the small amount of ferric iron in the ferrous chloride solution and traces of interfering impurities in the reagents by running a blank under the same conditions as the sample, and make the necessary correction. Calculate the nitroglycerol from the amount of ferrous chloride required to reduce it.

If 2,4-dinitrotoluene is present it may be determined in the solution at this stage. Add a 100 % excess of titanous chloride solution, again connect the flask to the condenser, boil for five minutes, cool as before, and titrate the excess of the reducing agent with standard ferric alum.

Run a blank determination, adding equal quantities of the reagents, and having ascertained the slight loss of titanous chloride on boiling, apply the proper correction in calculating the results.

The ammonium thiocyanate has no effect upon the reaction according to Becker. The ferrous chloride will not reduce the 2,4-dinitrotoluene as long as some ferric ion is present, and ferric iron is formed as soon as reduction begins.

V. EXPERIMENTAL

A. Apparatus.

The apparatus used was essentially that of Knecht and Hibbert as modified by English and Thornton and Chapman. The titanous chloride was stored under hydrogen in the storage bottle of red-brown glass (c) (Fig. 2) . The hydrogen was furnished by a Kipp generator (a) charged with zinc and 6 N sulfuric acid with a little copper sulfate which acts as a catalyst. The hydrogen is cleansed of impurities which would react with titanous chloride by passing through a large wash bottle containing a concentrated solution of titanous chloride in a 20 % sodium citrate solution. This was suggested by Kolthoff and Robinson (III APPARATUS). A similar wash bottle is used in the carbon dioxide line. They are represented in the Figure by (b) and (b') respectively. It is well to have two of them in tandem in a line to prevent backing up of the titanous solution due to changes in temperature.

The storage bottle is fitted with a large stopper of rubber with three holes. One hole is for the lead-in tube for hydrogen. Another holds a glass tube leading to the top of the burette which allows equalization of pressure when the burette is filled. The third hole holds the siphon tube which extends to the bottom of the storage bottle inside it, and which leads to the bottom of the burette on the outside. It is connected to the burette (d) with a piece of pressure

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rubber tubing. The joint is wired,also. All joints and corks are shellaked care being taken to carry the layer of shellac out on to the glass to make a tight joint. The small rubber cork in the top of the burette containing the tube from the storage bottle is similarly treated.

The titration flask (e) is a 250-ml. Erlenmeyer flask fitted with a three-hole rubber stopper. One hole is for the burette tip and is kept plugged with a glass rod when solutions are heated or cooled during titrations. Another is for the entrance tube of the carbondioxide. The third holds a glass tube about eight inches long and bent in a right angle near the end which is in the cork. This tube is for the exit of the carbon dioxide and is of some length so as to prevent much back diffusion of air into the flask.

The carbon dioxide is taken from an ordinary pressure tank fitted with a reducing valve which will give a slow even flow of gas. It is rid of objectionable impurities in the same manner as the hydrogen.

The burette is an ordinary Exax grade burette with a side tube sealed on below the calibrations and above the stop-cock.

An ordinary reflux condenser fitted with a two-hole rubber stopper is used when compounds difficult to reduce are heated with the reducing agent. (h)

APPARATUS

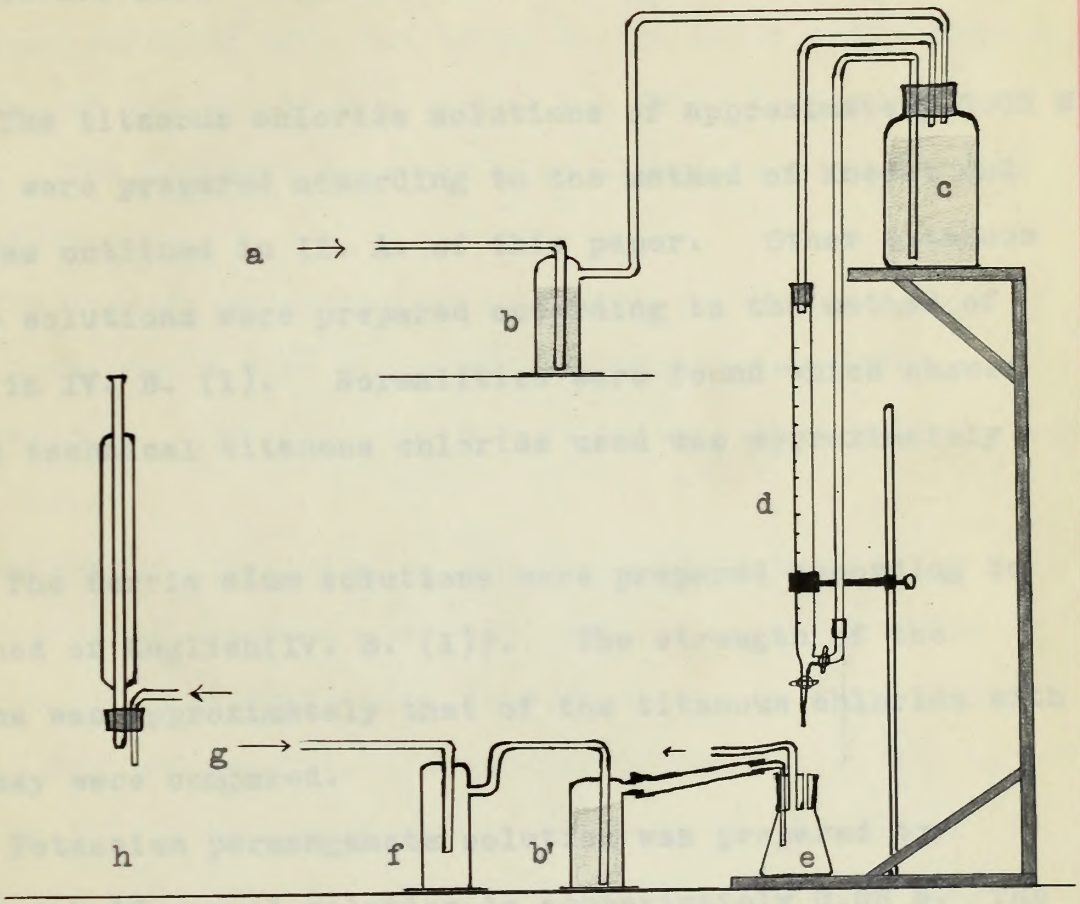
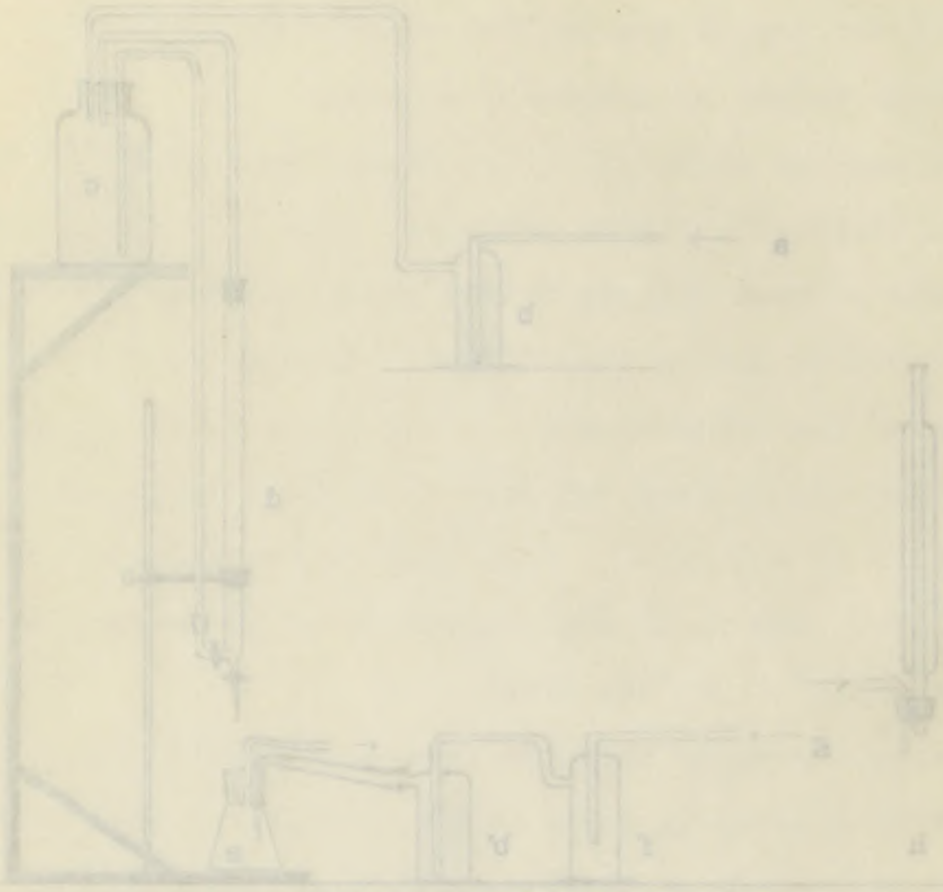


Figure 2.

(a) Kipp generator for hydrogen source.
(b) and (b') Wash bottles containing titanous chloride.
(c) Storage bottle of dark colored glass.
(d) Burette.
(e) Titration flask.
(f) Safety trap to protect valve from runback.
(g) Carbon dioxide tank.
(h) Condenser for compounds volatile in steam.



B. Preparation of Solutions.

All volumetric glassware was carefully calibrated and checked before use. Corrections were applied using recognized methods.

The titanous chloride solutions of approximately 0.03 N strength were prepared according to the method of Knecht and Hibbert as outlined in II. A. of this paper. Other titanous chloride solutions were prepared according to the method of English in IV. B. (1). Normalities were found which showed that the technical titanous chloride used was approximately 12 %.

The ferric alum solutions were prepared according to the method of English(IV. B. (1)). The strength of the solutions was approximately that of the titanous chloride with which they were compared.

Potassium permanganate solution was prepared by diluting a half-normal solution to approximately 0.08 N. The solution was boiled for several minutes and allowed to stand for a week. Then it was standardized against sodium oxalate in the standard way. The normality was found to be 0.07587. This solution did not change strength appreciably in two months.

The distilled water used in the titrations was prepared free from as much air as possible by boiling for 20 minutes in a two liter round-bottom flask and then cooling in an atmosphere of carbon dioxide. It was then kept in glass-

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The distilled water used in the titrations was prepared free from as much air as possible by boiling for 30 minutes in a two liter round-bottom flask and then cooling in an atmosphere of carbon dioxide. It was then kept in glass-

stoppered bottles.

The 40 % sulfuric acid used in the method of English was prepared from this boiled water. The required amount of concentrated sulfuric acid was added to the water while running carbon dioxide through it and having the flask immersed in an ice bath. The sulfuric acid was also stored in a glass-stoppered bottle.

Ten percent solutions of potassium thiocyanate and ammonium thiocyanate were prepared for indicators in the iron alum titrations. Ten ml. of 10 % solution give a satisfactory end-point color.

Methylene blue solution was prepared by making 9.5 g. of the "Medicinal" grade up to about 1800 ml. in distilled water which had previously been treated to remove dissolved air. A solution for indicator in the quinone determination was made by diluting this solution approximately 1 to 9. Two drops of this solution color 150 ml. of water distinctly blue. One drop may be used if the solutions are clear and colorless at the endpoint.

Ceric sulfate was prepared according to the directions of Smith (1),whose preparation was used. Sixty-seven grams of anhydrous ceric sulfate are placed in a 600-ml. beaker and 28 ml. of concentrated sulfuric acid are added. The mixture is then diluted with water (28 ml.), and then heated and stirred

(1) Smith, Ceric Sulfate, p. 52. (1933)
G. Frederick Smith Chemical Co., Columbus, Ohio.

until the salt dissolves. More water may need be added. This solution was made up to two liters as an approximately 0.05 N solution was desired. Standardized against sodium oxalate, the solution was found to be 0.05547 N.

Methyl red for indicator in ceric sulfate titrations was made up using 0.2 g. of the salt in 100 ml. of 6 N sulfuric acid. This was found to be too strong and the solution was then diluted to 500 ml.

The ferrous o-phenanthroline complex indicator for ceric sulfate titrations was made according to the directions given by Smith (1). Walden, Hammett, and Chapman developed (2) this oxidation indicator which had been discovered by Blau in 1898. The ferrous sulfate solution was made by dissolving .348 g. of the ferrous sulfate hydrate (7HOH) in 25 ml. of water. To this solution was added slowly with stirring a solution of 0.743 g. of the O-phenanthroline in 25 ml. of water. Stirring was continued until all solid material dissolved.

The ICl catalyst used in the standardization of the ceric sulfate with sodium oxalate was prepared according to the directions of Jamieson (3). The following materials are required: potassium iodide C. P.; potassium iodate C. P.; chloroform; hydrochloric acid, sp. gr. 1.18; a dilute solution

(1) Smith, Ceric Sulfate. p. 54. (1933)
G. Frederick Smith Chemical Co., Columbus,-Ohio.

(2) Walden, Hammett, and Chapman,
J. A. C. S., 53, 3908 (1931)

(3) G. S. Jamieson, Volumetric Iodate Methods, p. 89.
The Chemical Catalog Co., New York. (1926)

of 0.005 M potassium iodate (1.o7 g. in 1 liter of water); and a dilute solution of potassium iodide 0.01 M (1.66 g. in 1 liter of water).

Procedure:
Dissolve 10 g. of potassium iodide and 6.74 g. of potassium iodate in 90 ml. of water. The solution should not liberate iodine. Add 90 ml. of concentrated hydrochloric acid and stir well. The reaction:

2KI plus KIO_3 plus 6HCl equal 3KCl plus 3ICl plus 3HOH

If potassium iodide has been added in excess, this must be reacted by the addition of just the correct amount of potassium iodate. The solution will become orange colored. Add 5 ml. of chloroform and stir. If potassium iodide has been added in excess, the chloroform will be colored purple. Add potassium iodate a few drops at a time until the chloroform is colored only very faintly after vigorous stirring. Titrate back and forth over the end-point to be sure of the proper color. The solution is 0.5 M in ICl. Ten ml. of this solution diluted to 1000 ml. are used in 5-10 ml. portions as a catalyst in ceric sulfate titrations. Solutions of ICl should be stored in colored, glass-stoppered bottles in the dark.

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$5KI$ plus KIO_3 plus $6HCl$ equal $3XCl$ plus $3ICl$ plus $3H_2O$

If potassium iodide has been added in excess, this must be removed by the addition of just the correct amount of potassium iodate. The solution will become orange colored. Add 3 ml. of chloroform and stir. If potassium iodide has been added in excess, the chloroform will be colored purple. Add potassium iodate a few drops at a time until the chloroform is colored only very faintly after vigorous stirring. Titrate back and forth over the end-point to be sure of the proper color. The solution is 0.3 M in ICl. Ten ml. of this solution diluted to 1000 ml. are used in 5-10 ml. portions as a catalyst in cerio sulfate titrations. Solutions of ICl should be stored in colored glass-stoppered bottles in the dark.

C. Standardization of Solutions.

The primary standard in the earlier determinations is sodium oxalate. The standard potassium permanganate was checked against that standard. The usual quantitative procedure was used. The primary standard in the later determinations is also sodium oxalate, but the secondary standard is ceric sulfate. It will we seen that these standards do not give the same normalities because the ferric alum cannot oxidize the ferrous iron in the titanous chloride as does the ceric sulfate. They agree well in the final result, however, and also with a standard solution of pure p-nitroaniline.

The ferric alum is standardized against the potassium permanganate using the stannous chloride reduction and the titration according to the well established method of Zimmerman and Reinhardt. Corrections are made for all endpoints according to blanks run under similar conditions. Normalities 0.06592, 0.06595, 0.06583, 0.06588, and 0.06593 give an average of 0.06590 N for the ferric alum. This was found to change very slightly in a month. Therefore, the next ferric alum solution was oxidized to a very faint pink with potassium permanganate solution before standardization. This second solution gave 0.04816 N and later 0.04819 N by standard permanganate. Using the following method by ceric sulfate the iron alum gave a normality of 0.04810.

The method is a combination of methods in the literature and those in the pamphlet "Ceric Sulfate" published by G. Frederick Smith of the G. Frederick Smith Chemical Company, Columbus, Ohio. (1933) Second Edition.

Comparison of ferric alum with ceric sulfate:

To 30 ml. of 0.05 N (or 0.1 N) ferric alum solution add 5 ml. of 6 N HCl. Heat to boiling in a 500-ml. Erlenmeyer flask, keeping the flask in motion so that there will be no loss from sputtering. Add 0.05 N stannous chloride solution <u>one drop at a time</u> to the hot solution until all the ferric salt has been reduced, and one drop causes the color of the solution to change from yellow to colorless or very light yellow-green. During this time rotate the flask constantly and keep at boiling temperature. Add a drop of stannous chloride solution in excess. Add immediately 5 ml. of concentrated hydrochloric acid and rinse down the flask. Flush out the flask with a stream of carbon dioxide. Dilute with cold water to 250-300 ml. Add 10 ml. of saturated mercuric chloride solution. A slight, silky white precipitate will separate in about 2 minutes. In case a heavy precipitate forms, or no precipitate, discard the solution. Add 25 ml. of sulfuric-phosphoric acid mixture (150 ml. of each concentrated acid per liter of solution) and 0.05 ml. of methyl red indicator. (See V. B., p. 60) Titrate with the ceric sulfate until the red color is bleached out and the solution becomes very faint yellow. Correct for the end-point with blanks.

The end-point is distinct but faint and must be observed several times before it can be obtained accurately. The normality on permanganate was 0.04819 and on ceric sulfate 0.04810. The average of the figures for both methods gives 0.04815 N and this will be used in the calculations.

The ceric sulfate is easily standardized against sodium oxalate using ferrous o-phenanthroline as indicator. The method of Willard and Young was used. (1)

The method: (for 0.05 to 0.06 N solutions)

Weigh accurately to at least four places 0.11 to 0.12 g. of pure sodium oxalate and place in a 400-ml. beaker. Dissolve by the addition of 20 ml. of concentrated HCl diluted to 95 ml. Stir until dissolved and add 5 ml. of 0.005 M ICl solution and heat to 50 degrees C. Use a thermometer as a stirring rod, and after the addition of one drop of 0.025 M ferrous O-phenanthroline complex, titrate with ceric sulfate until the solution is pale blue in color and there is no return of any pink color during the interval of one minute. If the temperature falls below 45 degrees C., heat the solution to 50 degrees C. again. The normality is easily calculated:

$$\text{Normality equals} \quad \frac{\text{weight of oxalate}}{(0.06700)\ (\text{ml. of } Ce(SO_4)_2 \text{ used})}$$

Four titrations using samples of sodium oxalate ranging from 0.0796 g. to 0.1381 g. varied through a range of only 2 parts in 5000. The average normality was found to be 0.05547 N.

(1) Smith, Ceric Sulfate. p. 57. (Described above)

The titanous chloride solution is checked against an iron alum or any other solution with which it reacts quantitatively, before each determination. A standard solution of ceric sulfate was found convenient to standardize and to check the titanous chloride against.

Using hydrochloric acid and a procedure similar to that of Knecht and Hibbert:

Measure out accurately 25 ml. of ferric alum into the titration vessel and put in the special stopper after adding 25ml. of water and 10 ml. of concentrated hydrochloric acid. Flush with a stream of carbon dioxide for five minutes. Add 10 ml. of potassium thiocyanate for indicator. Titrate with titanous chloride until the solution remains colorless for 30 seconds. The normality obtained will be used in those titrations in which the solutions are not boiled in the reductions. If the material to be estimated requires that the solution be kept at boiling temperature for several minutes, the standardization is carried out in the other direction adding the iron alum to the titanous chloride. The titanous chloride solution is treated in the same manner as it is treated in carrying out a determination.

Using sulfuric acid,

Measure 25 ml. of 40 % sulfuric acid into the titrating vessel and add about 10 ml. of air-free distilled water to offset loss in heating. Replace the stopper and run a stream of carbon dioxide through the vessel for three or four minutes.

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Using sulfuric acid.

Measure 25 ml. of 40 % sulfuric acid into the titrating vessel and add about 10 ml. of air-free distilled water to offset loss in heating. Replace the stopper and run a stream of carbon dioxide through the vessel for three or four minutes.

Run out four or five drops from the titanous chloride burette (run out all past the stop-cock if the burette has not been used for some time) to make sure that the air has not reacted appreciably with any used in the determination. Quickly connect the titration flask and continue the stream of carbon dioxide for another minute. Run out 25 ml. of titanous chloride. Heat just at boiling for five minutes. Cool in an ice bath being careful that the carbon dioxide stream is swift enough to prevent the entrance of air. Titrate to the disappearance of the purple color with standard iron alum, add 10 ml. of 10 % potassium thiocyanate by means of a pipette through the stopper, and then titrate to a red color permanent for 30 seconds.

Using ceric sulfate in place of ferric alum;

The titration is carried out exactly the same as with ferric alum except that one drop of the ferrous o-phenanthroline complex solution is added as indicator just after the solution is cooled. The solution is titrated directly with ceric sulfate until all the red color leaves and the solution becomes a very faint yellow-blue in color. The end-point is distinct and stable. The solution begins turning color a few drops before the end-point. If the titanous solution contains ferrous iron, it will also be titrated and the normality will appear higher than that obtained using ferric alum. In those titrations in which ceric sulfate can be used in the back titration, this causes no error.

If iron alum must be used in the back titration, the amount of iron in the titanous chloride solution may be determined once and for all from the difference in the two titers, and this correction applied. I suggest this procedure because the ceric sulfate is so easily and accurately standardized and because the titration of titanous chloride with ceric sulfate is more satisfactory than with ferric alum. The difficulty may be overcome by using iron free titanous chloride. There are several nearly iron free preparations on the market.

Methylene blue is standardized against the titanous chloride. A measured amount of the solution is run into the titration flask, 10 ml. of concentrated HCl and 25 ml. of air-free water are added, and a stream of carbon dioxide is allowed to run through the flask for several minutes. The contents are heated to 35 degrees (or add one drop of a 10 % solution of sodium salicylate) and titanous chloride is run in until the color just disappears.

D. Determinations.

1. Quinone.

Benzoquinone was reduced to hydroquinone by direct titration with titanous chloride using methylene blue as an indicator and heating the solution to 35 degrees.

The reaction:

$C_6H_4O_2$ plus 2 $TiCl_3$ plus 2 HCl equals $C_6H_6O_2$ plus 2 $TiCl_4$

The quinone was recrystallized from alcohol, steam distilled, and then recrystallized from alcohol. The melting point was 112.5 degrees and it was sharp. This is several degrees lower than the value 115.7 degrees usually given.

The method used in the reduction was essentially that of Knecht and Hibbert (1). A solution of quinone in air-free distilled water was made up containing 0.0019266 g. per ml. at 20 degrees. A known amount was measured into the titration flask, 5 ml. of concentrated hydrochloric acid added, a drop of methylene blue solution added for indicator, the volume made up with water to about 100 ml., the solution warmed to 35 degrees, and the air driven out of the system with carbon dioxide. The solution was titrated directly with titanous chloride solution keeping the temperature at 35 degrees, until the color was completely bleached out. A blank was run for correction of the end-point. The titanous chloride was

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New Reduction Methods in Volumetric Analysis, Second Edition (1925) p. 40, 8, 96. Longmans,Green and Co., London.

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New Reduction Methods in Volumetric Analysis, Second Edition (1925) p. 40, 8, 96. Longmans,Green and Co., London.

standardized in an exactly similar manner just before the determination, giving normalities compared with ferric alum of 0.05828 and 0.05833. The average was 0.05831 N.

Three runs gave the following purities:

98.97 %, 98.89 %, and 99.26 %; average of 99.04 %. This is a 0.22 % variation from the average.

2. p-Nitroaniline.

Any o-nitroaniline in the sample was removed by forming the hydrochloride with hydrochloric acid, cooling in ice, and filtering in a funnel containing ice. The p-nitroaniline was then recrystallized twice from a methyl alcohol-water mixture twice. It melted sharply at 147 degrees C. All temperatures will be given in Centigrade. It was then recrystallized from water and the melting point remained at 147 degrees. Richter and Norris both give 147 degrees for the melting point. Callan and Henderson in the work reviewed above give 149.5 degrees. This must be a corrected reading.

A solution of the salt was made up containing 0.001561 g. per ml. at 20 degrees. The salt was dissolved in hydrochloric acid and made up with distilled water. A portion of the solution was accurately measured into the titration flask, 25 ml. of 40 % sulfuric acid added, the flask connected to the titanous chloride burette, and the air swept out by a rapid stream of carbon dioxide for five minutes. (The tip of the burette must be freshly filled.) An accurately measured amount of titanous chloride (about 50 ml.) was added.

The flask was removed, the hole for the burette stoppered, and the solution brought just to boiling and kept there for five minutes. The rate of flow of the carbondioxide is reduced during heating and increased during cooling. The flask was then removed from the triangle and cooled in an ice bath. If the volume had decreased appreciably, distilled air-free water was added through the stopper from a pipette. The flask was connected to the iron alum burette and iron alum added until the violet color just faded. Then 10 ml. of 10 % potassium thiocyanate were added as indicator, using a pipette through the stopper. The flask was then connected again to the iron alum burette and titration continued to a faint pink permanent for 30 seconds.

Two concentrations of titanous chloride were used. Using the dilute solution, 0.03429 N, 0.03426, 0.03424, and 0.03423 N were the normalities obtained using ceric sulfate. No correction was made for ferrous iron because this solution was made from a nearly iron-free product. The average normality of the titanous chloride was 0.03425 N.

Seventeen ml. of p-nitroaniline solution containing 0.001156 g. per ml. required 24.99 ml. of 0.03425 N. titanous chloride for reduction giving a purity of 100.2 %. Ceric sulfate was found unsatisfactory for the back titration in this estimation. Using 0.06201 N titanous chloride, two determinations gave 101.1 % and 101.1 %. Corrected for the average loss of the titanous chloride on heating at boiling

temperature for 5 minutes these determinations become the same as the former determination, 100.2 %. The correction needs be applied because the normality 0.06201 was taken using cold solutions. This normality changed to 0.06167 in 12 days taken cold for comparison. The storage bottle was about half full at the time. This is a decrease of 0.55 %. The solution decreases much faster in strength after the bottle is nearly used up. The results show that p-nitroaniline is a satisfactory standard for titanous chloride.

3. p-Nitrosodimethylaniline.

p-Nitrosodimethylaniline was recrystallized once from ligroin and upon drying in the air and then in a vacuum desiccator gave a melting point of 85.5 degrees. A solution containing 0.002260 g. per ml. was made dissolving the salt in hydrochloric acid and diluting with water.

The same procedure was used for the estimation as with the p-nitroaniline. The solution was heated only to 70 degrees and not to boiling in the reduction. The titanous chloride was standardized in the same manner.

In the first determination, 21.52 ml. of p-nitroso-dimethylaniline containing 0.002260 g. per ml. required 19.55 ml. of 0.06095 N titanous chloride for reduction. The amount of compound was found to be 91.9 %. In the second, 20.32 ml. required 18.53 ml. of titanous chloride. This gives 92.25 %. The average purity was found to be 92.1 %.

After standing several days the p-nitrosodimethylaniline solution turned red. Ferric alum was used in the standardization of the titanous chloride and in the back titrations. Ceric sulfate was tried in the back titration of the excess titanous chloride but a satisfactory end-point using the ferrous o-phenanthroline complex indicator could not be obtained.

4. Azobenzene.

A good grade azobenzene was treated in solution with boneblack and filtered. The crystalline product was recrystallized from an alcohol-water mixture and dried in a vacuum desiccator containing calcium chloride and desicchlora. The product melted sharply at 68 degrees. A solution was made up containing 0.052745 g. per 25 ml. in pure alcohol.

As the azobenzene is volatile with steam, the titration flask was connected to a condenser fitted with a two-hole rubber stopper during the reduction. The carbon dioxide was let in through a glass tube in the one hole.

A 25 ml. portion was pipetted into the titration vessel and the stopper attached. Carbon dioxide was allowed to flow through the vessel for five minutes. During this time 25 ml. of 40 % sulfuric acid were added through the stopper. Then excess (50 ml.) of titanous chloride were added and the flask connected to the condenser. The solution was gently refluxed for 6 min. The excess titanous chloride

was titrated with ferric alum. The potassium thiocyanate (10 ml. of 10 %) was added when near the end-point.

The azobenzene taken, 25 ml. of solution containing 0.052745 g., required 9.95 ml. of 0.05788 N titanous chloride for reduction. Therefore the reduction proceeds as follows:

$C_6H_5N \overset{6}{=} NC_6H_5$ plus 2 $TiCl_3$ plus 2 HCl equals

$C_6H_5NH - NHC_6H_5$ plus 2 $TiCl_4$

The calculation on this basis gives 99,42 % pure.

Carrying out the titration in a similar manner with stronger titanous chloride, not using the condenser but adding the alcoholic solution directly to the titanous chloride solution kept at the boiling point, adding the solution by means of a pipette through the stopper, the azobenzene was found to be reduced with but slight loss.

Twenty-five ml. of the solution of azobenzene required 9.18 ml. of 0.06095 N titanous chloride for reduction. This gives a purity of 96.8 %.

Ceric sulfate was used in the back titration with the ferrous o-phenanthroline complex as indicator in an estimation carried out in the same manner as the above. The solution was orange red during the titration and gradually became deeper in color and seemed to become magenta. The end-point was met with a brown-yellow color.

Twenty-five ml. of the azobenzene solution required 9.12 ml. of 0.06146 N (to ceric sulfate) titanous chloride.

The equivalent weight of the azobenzene is 91.05 as it requires two equivalents of hydrogen for reduction. Therefore one ml. of the normal solution would contain 0.09105 g.

The amount of azobenzene found equals

(9.12) (0.06146) (0.09105) equals 0.05104 g.

The amount taken was 0.05275 g.

Therefore the compound must be $\frac{0.05104}{0.05275}$ or 97.0 % pure assuming no loss from volatilization with steam. This agrees well with the value obtained using ferric alum in the back titration.

5. Citral.

A solution of citral was made up with alcohol containing 1.0123 g. of citral in 500 ml. final volume. The citral was weighed by difference using a weighing pipette. In each estimation 25 ml. of this solution were used.

Using the ordinary method of English but continuing the heating for 8 minutes instead of 5, 5.05 % of the citral was reduced assuming both double bonds were attacked. The vapor of the citral was quite strong in the atmosphere and much of it was lost. The condenser was then used during the reduction and the heating continued for 15 minutes. The amount of reduction was only slightly greater, 7.61 %. These values are doubled if only one double bond is attacked.

In each case the same amount of alcohol was added to the reduction solution during the standardization of the titanous chloride in order to compensate for any reduction of the alcohol or impurities in it. It is evident from the results given that this is not a promising quantitative reaction.

5. Citral.

A solution of citral was made up with alcohol containing 1.0125 g. of citral in 500 ml. final volume. The citral was weighed by difference using a weighing pipette. In each estimation 25 ml. of this solution were used.

Using the ordinary method of English but continuing the heating for 8 minutes instead of 5, 5.05 % of the citral was reduced assuming both double bonds were attacked. The vapor of the citral was quite strong in the atmosphere and much of it was lost. The condenser was then used during the reduction and the heating continued for 15 minutes. The amount of reduction was only slightly greater, 7.81 %. These values are doubled if only one double bond is attacked.

In each case the same amount of alcohol was added to the reduction solution during the standardization of the titanous chloride in order to compensate for any reduction of the alcohol or impurities in it. It is evident from the results given that this is not a promising quantitative reaction.

6. Nitrosodiethylamine.

A solution of nitrosodiethylamine was made up with distilled water containing 1.0558 g. in 500 ml. of solution. 25 ml. of this solution were used in each determination. The method of English was used thoughout and the solutions heated for 6 minutes. Reduction was found to be less than 2 %. No appreciable reduction was obtained on a 10 ml. portion boiled for 10 minutes in a more concentrated titanous chloride solution. The compound does not appear to be attacked by a dilute solution of titanous chloride.

7. p-Nitrobenzeneazoresorcinol-2,4.

The sample of p-nitrobenzeneazoresorcinol-2,4 melted at 195-196 degrees C. Richter gives 199-200 degrees C. No suitable solvent was found for making up a solution of the compound. Samples were weighed out into 250-ml Erlenmeyer flasks which served for titration flasks. The samples were dissolved in 7 ml. of concentrated sulfuric acid and 40-50 ml. of water was added just before the addition of the excess titanous chloride. This precipitated the compound in a very fine state of subdivision and in this state it was attacked by the titanous chloride. It could not be powdered fine enough to react completely in the titanous chloride reduction solution. The compound was estimated from this point on by the usual procedure in the method of English. It was found that reduction was most satisfactory when the solution was heated just at boiling for 8 minutes under the reflux condenser. Reduction of from 60 to 80 % was obtained without the use of the condenser. Samples ranged from 30 to 60 mg. A 35 mg. sample is recommended.

After much experimentation and practice in technique of changing the flask on the condenser, the following purities were found based on freshly restandardized solutions:

100.8 %, 98.7 %, and 99.44 %; average 99.65 %.

The p-nitrobenzeneazoresorcinol was quantitatively reduced requiring 10 equivalents of titanous chloride.

8. p-Nitrobenzeneazo-beta-naphthol.

p-Nitrobenzeneazo-beta-naphthol was twice recrystallized from toluene and gave a melting point of 249 degrees C. This is the melting point given in Mulliken. The recrystallization was carried out each time after the compound had been dissolved in hot toluene in a flask fitted with a reflux condenser.

In the estimation samples were weighed out into 250-ml. Erlenmeyer flasks as in the resorcinol compound above. From 30 to 45 mg. samples. The procedure used was the same in detail as that used for the p-nitrobenzeneazoresorcinol. Some trouble was encountered when the carbon dioxide reducing valve would not give an even flow of gas.

The reduction was found to proceed as expected with this type of compound the nitro group requiring six equivalents of titanous chloride and the azo group requiring four. Both go to amino groups.

Three determinations gave:

96.2 %, 98.1 %, and 100.6 %; average 98.3 %.

Therefore the p-nitrobenzeneazo-beta-naphthol is quantitatively reduced by a dilute titanous chloride solution.

VI SUMMARY

A review of the literature in the field of the reduction of organic compounds by the use of titanous chloride has been given. The work of Knecht and Hibbert, the pioneer work in the field, has been summarized. It has been shown that their method of standardizing the solution and of estimating compounds fulfill the ordinary requirements in the analytical laboratory. Their use of ferric alum in the back titrations in the indirect methods was found satisfactory and this method is yet the most satisfactory one. A solution of titanous chloride of from 0.05 N to 0.1 N in strength is recommended in place of the weaker solution of Knecht. The apparatus of Knecht and Hibbert is described.

The method of English introduces greater precautions in the preparation and the protection of the solution and is recommended for accurate work. It is especially adapted to use with the aromatic nitro compounds. The relatively concentrated sulfuric acid reduction medium helps prevent side reactions. It gives a slightly more distinct endpoint in the standardization with ceric sulfate.

The advantage of reduction in the cold and hence less decomposition of the titanous chloride in the method of Kolthoff and Robinson using a solution of 20 % strength in sodium citrate is offset by the need of making a correction for the action of the titanous salt on the sodium citrate.

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Becker's ingenious method for the estimation of nitroglycerol and nitroglycerol and dinitrotoluene in admixture is given. The nitroglycerol is reduced with ferrous chloride in an atmosphere of carbondioxide and the dinitrotoluene is then titrated with titanous chloride.

Most of the improvements in apparatus and technique have been incorporated into the method of estimation used and a diagram is given of the apparatus. Methods are for the most part, modifications of the method of English. His method was also used in the preparation of the stock titanous chloride.

Sodium oxalate was the primary standard. The titanous solutions were checked through permanganate and ferric iron and also ceric sulfate and ferric iron. Ceric sulfate is recommended for the standardization of the titanous solution. The ferrous o-phenanthroline complex is a splendid indicator in this reaction. The solution is red in the presence of titanous chloride and very light yellow-blue in the presence of a very slight excess ceric sulfate. The end-point is sharp and only 0.02 ceric sulfate (0.05 N) (in ml.) is required to oxidize the drop of indicator.

Quinone, p-nitroaniline, and p-nitrosodimethylaniline were determined in modifications of the usual methods. Azobenzene was reduced quantitatively and both ferric alum and ceric sulfate used in the back titration. No mention is made in the literature of this reduction being done quantitatively. Ceric sulfate was found unsatisfactory in titrating the excess

titanous chloride in the reduction of quinone, p-nitroaniline, and p-nitrosodimethylaniline. p-Nitroaniline gave nearly theoretical results. This is in agreement with English, who used it for a standard.

Citral and nitrosodiethylamine were found not to be reduced more than a few percent even with the use of the reflux condenser during the reduction.

p-Nitrobenzeneazoresorcinol-2,4 and p-nitrobenzeneazo-beta-naphthol were found to be quantitatively reduced by titanous chloride when in a very fine state of subdivision. This state was obtained by adding the water required for a definite volume directly to a sulfuric acid solution of the above compounds.

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ABBREVIATIONS

Ann. ----------	Annalen der Chemie.
Ann. chim. anal. -----	Annales de chemie analytique.
Ann. chim. phys. -----	Annales de chemie et de physique.
Ber. ----------	Berichte der deutschen chemischen Gesellschaft.
Chem. Weekblad -----	Chemisch Weekblad.
Chem. Ztg. -----	Chemiker Zeitung.
Helv. chim. acta -----	Helvetica chimica acta.
Ind. Eng. Chem. -----	Journal of Industrial and Engineering Chemistry.
Ind. Eng. Chem., Anal. Ed.	-----, Analytical Edition.
J. A. C. S. -----	Journal of the American Chemical Society.
J. C. S. ----------	Journal of the Chemical Society (London) (English)
J. S. C. I. -----	Journal of the Society of Chemical Industry.
J. S. D. and C. -----	Journal of the Society of Dyers and Colorists.
Rec. trav. chim. -----	Recueil des travaux chimiques.
Z. anal. Chem. -----	Zeitschrift für analytische Chemie.
Z. anorg. allgem. Chem.	Zeitschrift für anorganische allgemeine Chemie.
Z. Elektrochem. -----	Zeitschrift Elektrochemie.
Z. physik. Chem. -----	Zeitschrift für physikalische Chemie.

ABBREVIATIONS

Ann. ----------	Annalen der Chemie.
Ann. chim. anal. -----	Annales de chemie analytique.
Ann. chim. phys. -----	Annales de chemie et de physique.
Ber. ----------	Berichte der deutschen chemischen Gesellschaft.
Chem. Weekblad -----	Chemisch Weekblad.
Chem. Ztg. -----	Chemiker Zeitung.
Helv. chim. acta -----	Helvetica chimica acta.
Ind. Eng. Chem. -----	Journal of Industrial and Engineering Chemistry.
Ind. Eng. Chem., Anal. Ed. -----,	Analytical Edition.
J. A. C. S. -----	Journal of the American Chemical Society.
J. C. S. ----------	Journal of the Chemical Society (London) (English)
J. S. C. I. -----	Journal of the Society of Chemical Industry.
J. S. D. and C. -----	Journal of the Society of Dyers and Colorists.
Rec. trav. chim. -----	Recueil des travaux chimiques.
Z. anal. Chem. -----	Zeitschrift für analytische Chemie.
Z. anorg. allgem. Chem.	Zeitschrift für anorganische allgemeine Chemie.
Z. Elektrochem. -----	Zeitschrift Elektrochemie.
Z. physik. Chem. -----	Zeitschrift für physikalische Chemie.

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